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# Carbonate clumped isotope analysis ($\Delta_{47}$) of 21 carbonate standards determined via gas source isotope ratio mass spectrometry on four instrumental configurations using carbonate-based standardization and multi-year datasets

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Keywords: carbonate clumped isotope geochemistry, stable isotopes, clumped isotopes

Abstract:

**Rationale:** Clumped isotope geochemistry examines the bond ordering of rare, heavy isotopes in molecules and provides information about the thermodynamic and kinetic controls on their formation. Since the first clumped isotope measurements of carbonate minerals were published 15 years ago, interlaboratory offsets in calibrations have been observed, and laboratory and community practices for measurement, data analysis, and instrumentation have evolved. Here we briefly review historical and recent developments for carbonate clumped isotope measurements, test a recently published proposal for carbonate-based standardization on multiple instruments using multi-year datasets, and report values for 21 different carbonate standards that allows for recalculations of previously published datasets.

**Methods:** We examine data from 4628 standards analyzed over a 4 year interval on Thermo MAT 253 and Nu Perspective IS mass spectrometers, using common acid bath and small sample individual reaction vessels. Each configuration was analyzed by treating some standards as working standards and the remainder as unknowns (consistency standards).

**Results:** We show that acid digestion systems using either individual reaction vessels at 70°C or a common acid bath at 90°C, as well as different mass spectrometer models, yield indistinguishable results when instrument drift is well characterized. For the linearity correction, the implementation of mixed gas-and-carbonate standardization or carbonate-only standardization yield similar results. No difference is seen in the use of either 3 or 8 working standards for the construction of transfer functions.

**Conclusions:** We expanded the number of instrumental configurations utilized for intercomparison beyond prior work, and show all configurations yield similar reproducibility if instrument drift is robustly characterized and either carbonate- or mixed gas-and-carbonate-based standardization is used. $\Delta_{47}$ values are reported for 21 carbonate standards, facilitating the intercomparison of data from a diversity of labs and instrument configurations, and the restandardization of a broad range of sample sets generated between 2006 to present.

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# Carbonate clumped isotope analysis ($\Delta_{47}$) of 21 carbonate standards determined via gas source isotope ratio mass spectrometry on four instrumental configurations using carbonate-based standardization and multi-year datasets

*Rapid Communications in Mass Spectrometry*

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*Running Head: Carbonate Clumped Isotope Analysis of 21 Carbonate Standards via IRMS*

**Rationale:** Clumped isotope geochemistry examines the pairing or clumping of rare, heavy isotopes in molecules and provides information about the thermodynamic and kinetic controls on their formation. Since clumped isotope measurements of carbonate minerals were first published 15 years ago, interlaboratory offsets in calibrations have been observed, and laboratory and community practices for measurement, data analysis, and instrumentation have evolved. Here we briefly review historical and recent developments for carbonate clumped isotope measurements, test a recently published proposal for carbonate-based standardization on multiple instruments using multi-year datasets, and report values for 21 different carbonate standards that allows for recalculations of previously published datasets.

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## 1. INTRODUCTION

The field of clumped isotope geochemistry is based upon the abundances of multiple rare heavy isotope substitutions in molecules, including $CO_2$ (e.g., $^{13}C^{18}O^{16}O$), dissolved inorganic carbon species, carbonate minerals, and methane (1, 2, 3, 4). Equilibrium fractionations of multiply-substituted molecular species are governed by temperature-dependent homogeneous isotope exchange reactions (3, 5, 6, 7). The most widely studied system in clumped isotope geochemistry is based on the proportion of $^{13}C$ and $^{18}O$ isotopes bound to each other within carbonate ion ($^{13}C^{18}O^{16}O_2^{2-}$) groups in carbonate-containing minerals, relative to a stochastic distribution of isotopes (1, 2, 3, 6, 7). Carbonate clumped isotope thermometry has been used to probe the temperature history of surface (8) and subsurface environments (9), paleo-physiology (10), biomineralization processes (11), the alteration history of meteorites (12, 13, 14), as well as the origin of possible kinetic effects (3, 15).

However, a range of instrumentation and techniques have been employed by different labs. Several studies comparing a breadth of instrumentation have identified factors that contribute to inter-lab offsets and proposed advances to address inter-comparability (16, 17, 18, 19). In addition, community-wide changes in standardization methods have occurred (16), in addition to laboratory-specific practices (17). Building on this work, we implement a recent proposal from Bernasconi et al. (2018) of utilizing carbonate standardization for reference frame construction (as initially described in Dennis et al., 2011). We utilize and build upon this suggested standardization approach on a multi-year dataset (n = 4628) from multiple instruments and digestion systems to explore the efficacies of different implementations.

The lab at UCLA is uniquely situated to do this as it employs both the pioneering instrumentation that is widely used (Thermo MAT 253) and the newest generation of mass spectrometers (Nu Perspective IS). The Thermo MAT 253 is paired with a common acid bath digestion system for large samples containing 3-6 mg of pure carbonate (20). The Nu Perspective IS has advancements including secondary electron suppression and continuous pressure balancing. These advancements allow for the use of both a small (0.25-0.5 mg of pure carbonate) single-sample digestion system (the Nu Carb device), and a common acid bath sample digestion system designed and fabricated in our lab.

The main contribution of this study is presenting standard values for 21 internal and international carbonate standards run on multiple mass spectrometer systems. We demonstrate the stability of different types of instruments, showing that considerable drift can occur on timescales of more than a month, consistent with a recent report by Defliese and Tripati (2020). We also find that carefully chosen measurement windows associated with frequent analysis of standards are necessary to yield results that are comparable across multiple instruments. Consistent with Bernasconi et al. (2018), we show that convergent results can be achieved using all acid digestion setups, acid temperatures, samples sizes, mass spectrometer models, and standardization procedures. These results are promising for future widespread applications of clumped isotope analyses, as we expand the number of instrumental configurations beyond what has been utilized previously. The breadth of standards reported allows for intercomparison of data from a diversity of labs and instrument configurations, and the restandardization of a broad range of sample sets.

## 2. BACKGROUND

### 2.1 Explanation of the Carbonate Clumped Isotope Thermometer

In carbonate minerals and dissolved inorganic carbon (DIC) species, heavy isotopes $^{13}C$ and $^{18}O$ are rare relative to light isotopes, $^{12}C$ and $^{16}O$. Combinations of these isotopes form isotopologues of carbonate ions with masses varying from 60 to 67 amu. Acid digestion of carbonate minerals with these isotopologues produces $CO_2$ isotopologues of masses 44 to 49 amu with abundances related to their abundances in the solid prior to acid digestion (Supplementary Table 1) (1). Multiply substituted isotopologues of $CaCO_3$, DIC, and other molecules all have distinct properties due to distinguishable differences in zero point energy (1, 6). Therefore they serve as tracers of equilibrium and kinetic processes. While similar to the use of singly-substituted isotopes in many geochemical applications, the carbonate clumped isotope thermometer has the advantage of occuring within a single phase. Thus, carbonate minerals that form in equilibrium have a clumped isotopic composition that is only influenced by temperature (1, 2, 3, 6, 7, 13, 21, 22, 23).

For carbonate minerals, statistical thermodynamics predicts that the bonding or "clumping" of heavy isotopes $^{13}C$ and $^{18}O$ is negatively correlated with temperature (6). Heavy isotope bonding between $^{13}C-^{18}O$ will conform to isotopic equilibrium constants for reactions such as:

$$X^{12}C^{\mathbf{18}}\mathbf{O}^{16}O_2 + X^{\mathbf{13}}\mathbf{C}^{16}O_3 \rightarrow X^{\mathbf{13}}\mathbf{C}^{\mathbf{18}}\mathbf{O}^{16}O_2 + X^{12}C^{16}O_3{}^{2} \qquad [1]$$

where X refers to cations such as $Ca^{2+}$, $Mg^{2+}$, $Sr^{2+}$, $Ba^{2+}$ (6, 7, 8). The $^{13}C-^{18}O$ bond abundance in carbonate minerals can be measured using isotope-ratio gas-source mass spectrometry on $CO_2$ liberated from carbonates by reaction with phosphoric acid (1).

## 2.2 Notation

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$^{13}C-^{18}O$ bond ordering in $CO_2$ is described using the quantity $\Delta_{47}$: the deviation in the abundance of $CO_2$ molecules with a $m/z = 47$ from the abundance predicted by stochastic mixing. Several papers discuss calculation of isotope ratios in detail (7, 21, 24).

Briefly, the quantity $\Delta_{47}$ is dependent upon the abundance ratios of isotopologues $^{47}CO_2$, $^{46}CO_2$, and $^{45}CO_2$ relative to the major isotopologue $^{44}CO_2$ (21), denoted by $R_{47}$, $R_{46}$, and $R_{45}$. Because $R_{13}$ and $R_{18}$ are the ratios for $^{13}C/^{12}C$ and $^{18}O/^{16}O$, respectively, the isotopologue ratios $R_{47}$, $R_{46}$, and $R_{45}$ can be defined as:

$$R_{47} = (2\cdot R_{13}\cdot R_{18}) + (2\cdot R_{17}\cdot R_{18}) + (R_{13}(R_{17})^2) \qquad [2]$$

$$R_{46} = (2\cdot R_{18}) + (2\cdot R_{13}\cdot R_{17}) + (R_{17})^2 \qquad [3]$$

$$R_{45} = R_{13} + (2\cdot R_{17}) \qquad [4]$$

Given that $\Delta_{47}$ is defined as the excess of $^{13}C^{18}O^{16}O$ in a sample relative to a stochastic abundance (denoted with a *), it can also be described as:

$$\Delta_{47} = [(R_{47}/R_{47}{*} - 1) - (R_{46}/R_{46}{*} - 1) - (R_{45}/R_{45}{*} - 1)]\cdot 1000$$
[5]

Expanded to include all terms, the quantity $\Delta_{47}$ is:

$$\Delta_{47} = \frac{R^{47}}{(2\cdot R13\cdot R^{18}) + (2\cdot R^{17}\cdot R^{18}) + (R^{13}(R^{17})^2)} - \frac{R^{46}}{(2\cdot R^{18}) + (2\cdot R^{13}\cdot R^{17}) + (R^{17})^2} - \frac{R^{45}}{R13 + (2\cdot R^{17})} + 1$$

$\Delta_{63}$ refers to the deviation in the abundance of the multiply-substituted $CO_3^{2-}$ isotopologue $^{13}C^{18}O^{16}O_2$ of $m/z = 63$ from the abundance predicted by random mixing. The $\Delta_{47}$ of a sample is related to the $\Delta_{63}$ of the same sample by correcting for isotopic fractionation that occurs during acid digestion, such that:

$$\Delta_{47} = \Delta_{63} + y \qquad [6]$$

where $y$ is the fractionation factor.

Bulk compositions of molecules with a $m/z = 47$ are reported relative to a reference gas standard, denoted by $\delta_{47}$:

$$\delta_{47}\ (‰) = (R_{47\text{-sample gas}}/R_{47\text{-reference gas}} - 1)\ \cdot 1000 \qquad [7]$$

Given the range of reference gases utilized by different laboratories as working gases, measured values of $\delta_{47}$ are not directly comparable between laboratories.

## 3. A REVIEW OF ANALYTICAL MEASUREMENTS AND DATA HANDLING

Huntington et al. (2009) gives an in-depth overview of the procedures used for determination of $\Delta_{47}$ ratios via mass spectrometry based on the procedures that were used 11 years ago. Here we describe briefly analytical measurements and data handling, as well as relevant literature for reference, and then describe in Section 4 the methods used in this study.

Briefly, mass spectrometric measurements of clumped isotope measurements of carbonates involve: The initial conversion of carbonate minerals to $CO_2$ by orthophosphoric acid digestion at a constant temperature. The product gases are purified to remove water, non-condensable gases such as $N_2$, $SO_2$, and organic compounds that are considered contaminants. Although there are variants with respect to methods, most methods use cryogenic purification to remove water and non-condensable gases, a trap or column with Porapak Q for organics, and silver wool for sulfur (1, 20, 24, 25). The abundances of $CO_2$ isotopologues 44 – 47 are determined using a gas-source isotope ratio mass spectrometer (1). Subsequent data handling includes corrections for $^{17}O$ and the bulk isotopic composition (26). Output from software associated with commercial mass spectrometers are processed using a diverse array of approaches, but may include Excel, scripts in R or other languages (19), and the community freeware "Easotope" (27). Results are standardized using equilibrated gas standards, carbonate standards, or both (1, 16, 17).

## 3.1 $^{17}O$, $^{18}O/^{16}O$, and $^{13}C/^{12}C$ definitions

The impact of using different parameter sets for the calculation of absolute isotope ratios (i.e., the $^{13}C/^{12}C$ ratio of VPDB, the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios of VSMOW or VPDB-$CO_2$, and the slope of the triple oxygen isotope line ($\lambda$)) was initially explored by Daeron et al. (2016), who showed this was a potentially important source of interlaboratory offsets for some laboratories. Their findings were partially validated by subsequent work for some instrumental configurations (28), but may not be as relevant to other configurations (19). The impact of the choice of parameter set depends in part on the composition of samples analyzed and the working gas used (19, 26). Best practices for these corrections include the use of the "Brand" parameter set(29) and are reviewed in depth by Daeron et al. (2016) and Petersen et al. (2019).

## 3.2 Using gas and/or carbonate standards for mass spectrometric corrections

Initially, clumped isotope measurements utilized 1000 $^{o}$C equilibrated gases of different bulk compositions that had stochastic distributions as working standards to implement a linearity correction (1, 26). Subsequent standardization approaches included multiple sets of heated and water equilibrated gases (16, 18, 19), use of carbonate standards (16, 17, 18), or a mixed gas and carbonate standards approach (18, 20), to implement both a linearity correction and a scale compression/stretching correction.

Mass spectrometric methods have changed since the first clumped isotope measurements of $CO_2$ were made 16 years ago (21), including with the implementation of different processes to correct for non-linearities in the measurement of multiply-substituted isotopic species. It is now understood that clumped isotope collectors have negative backgrounds arising from the presence of secondary electrons. These negative backgrounds are largely controlled by the flux rate of $CO_2$ to the ion source, and the resultant

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intensities of the ion beams (30). These negative backgrounds are typically statistically irrelevant in conventional analyses of singly-substituted isotopologues that yield $\delta^{18}O$ and $\delta^{13}C$ ratios, but are large compared to measured clumped isotope signals. Changes in mass spectrometer linearity due to pressure-dependent backgrounds can occur over short or long timescales (from weeks to months to years), and manifest as a dependence of the clumped isotope signal ($\Delta_{47\text{-WG}}$) on bulk isotopic composition ($\delta_{47\text{-WG}}$). To date, multiple methods are used for implementing these linearity corrections. Equilibrated gases are used by some labs to monitor the effects of changes in the negative background (1, 16, 21, 23, 24, 31), while others use measurements of the pressure-dependent background made by off-peak measurements (30, 32). Instruments with secondary electron suppression reduce the scale of these effects (18).

Investigation of inter-laboratory offsets led to the proposal of an absolute reference frame with a scale for $\Delta_{47}$ defined by the composition of gases equilibrated at two different temperatures (e.g., 25 and 1000 °C), that were pinned to theoretical calculations for thermodynamic equilibrium (16). It had been observed that on the stochastic reference frame, scale compression/stretching could occur, not only between instruments but on a single instrument, as noticed by the presence of drift in carbonate standard values over a timescale of months to years (e.g., see Fig. S4 in Passey et al., 2010). Thus, running equilibrated gases of two different bulk compositions and temperatures would allow for a linearity correction, and provide the basis for an additional scale compression/stretching correction (16). This work showed that the use of an absolute reference frame improved inter-lab reproducibility. Additionally, Dennis et al. (2011) suggested that carbonate standards could be defined in the absolute reference frame and used to develop secondary transfer functions (i.e. standardization based solely on carbonate standards), or a mixed transfer function (i.e. standardization based on a mixture of equilibrated gases and carbonate standards). Passey et al. (2010) utilized both gas and carbonate standardization. Analysis of carbonate standards also circumvents the challenge of treating samples and standards differently, which arises when only gases are used for reference frame calculations.

More recent work has suggested the use of carbonate standards for both linearity and scale compression corrections. Carbonates with a stochastic distribution and distinct bulk $\delta^{18}O$ and $\delta^{13}C$ compositions can be used for linearity corrections, such as the heating experiments producing the widely used carbonate standards ETH-1 and ETH-2 (17). This carbonate standards-based approach could be used instead of, or in addition to, the analysis of equilibrated gases. An additional carbonate standard with a much higher $\Delta_{47}$ (e.g., the unheated version of these standards), could be used to constrain scale compression/stretching, such as ETH-3 or ETH-4 (17), or other carbonate standards. Accurately pinning these values to the composition of equilibrated gases is critical for projection into the absolute reference frame.

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### 3.3 Acid digestion corrections

Acid digestion corrections are utilized to account for the range of different reaction temperatures used for clumped isotope measurements of carbonates (from 25 to 110 °C). Differences are observed between measured $\Delta_{47\text{-}25°\text{C}}$ and $\Delta_{47\text{-}70°\text{C}}$ (or digestion at any other temperature), and corrections are necessary to account for systematic offsets between materials digested at different temperatures. For oxygen isotopes, small but significant variations in acid digestion fractionation occur due to temperature, as well as digestion apparatus, acid density, grain size, mineral chemistry and structure, and acid:mineral ratio (30). These same factors are likely to be important for acid digestion fractionations of clumped isotopes, and thus acid digestion fractionations are the subject of several studies (1, 13, 25, 33, 34, 35).

A temperature-dependent acid fractionation factor (AFF) is usually added as a final step in the data reduction process (16) in order to help ensure values of $\Delta_{47}$ are comparable between laboratories (1, 13, 25, 33, 34, 35). Further, accounting for differences between $\Delta_{47}$ (determined on $CO_2$) and $\Delta_{63}$ (the value for the carbonate ion group) facilitates comparison with theory. $\Delta_{47}$-$\Delta_{63}$ offsets can be empirically determined using material from heating experiments (1, 13, 17) or theoretical values can be used(13).

We note that an acid digestion correction is, in principle, only necessary when equilibrated gases are used to build the absolute reference frame. Carbonate-based standardization can eliminate the need for acid digestion corrections, as the AFF is built into the reference frame. However, this is only the case if carbonate standard values are accurately defined in the absolute reference frame.

## 4. METHODS

We used two different types of mass spectrometer for clumped isotope measurements of $CO_2$ at UCLA: a 1) Thermo 253 isotope ratio mass spectrometer (IRMS) that is the most widely-used instrument for clumped isotope measurements, or a 2) Nu Perspective IS mass spectrometer with secondary electron suppression. We also have two different types of acid digestion and sample purification systems, and in all cases, reaction times, freeze-down temperatures, and transfer timings need to be determined. The different instrument configurations used in this study are described in Table 1.

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### 4.1 Phosphoric acid digestion and gas purification

### *4.1.a Common acid bath (CAB)*

The first type of digestion system used is a common acid bath system (CAB) modelled after what is described in Passey et al. (2010). Typical sample sizes range from 3-8 mg of pure $CaCO_3$, with larger amounts of sample required as $CaCO_3$ content decreases. The CAB systems we used were built in-house and modelled after what is used at Caltech and at Johns Hopkins University (20, 36). They include an automated, online digestion and $CO_2$ purification system (also referred to as an autoline). Briefly, an autoline is composed of:

(1) a Costech Zero Blank autosampler or custom-built Fairbanks device made of stainless steel that is capable of pulling high vacuum that can hold multiple samples;
(2) a common acid bath for phosphoric acid digestion of samples that are typically reacted for 20 minutes at a mineral-specific temperature (in our lab, typically 90 °C but ranging from 70-110 °C);
(3) cryogenic traps for removal of water and other gases with low vapor pressures, with one trap containing ethanol surrounded by dry ice and a second trap containing liquid nitrogen;
(4) an in-line Sigma-Aldrich elemental-silver wool column to remove sulfur compounds from the gas mixture;
(5) a Gas Chromatograph (GC) column using UHP Helium carrier gas, and Porapak Type-Q$^{TM}$ 50/80 mesh column packing material that maintains -20 °C during the gas transit to separate $CO_2$ from the remaining components of the produced gas mixture;
(6) a final cryogenic purification stage before transfer of $CO_2$ into the bellows of the mass spectrometer.

The use of a GC column packed with Porapak-Q and helium as a carrier gas enables this system to handle larger samples with significant organic content and smaller concentrations of pure carbonate, when compared to the other systems. Custom software was written in Labview to control the Autoline (the autosampler, all valves, the GC, and dewar lifters), and is coupled to the mass spectrometer control software (Thermo Fisher ISODAT software interface for the MAT 253; Perspective Stable Gas Control Software for the Nu Perspective).

### *4.1.b Nu Carb Sample Preparation System*

The second type of acid digestion system we use is a commercial Nu Carb Sample Digestion System that can react samples typically of 0.25 to 0.5 mg of pure $CaCO_3$. Samples are reacted for 20 minutes at 70 °C in individual reaction vials that eliminate potential memory effects from a common acid bath. This is similar to a Thermo Fisher Kiel device. The produced gases are then purified in a series of temperature-controlled, liquid-nitrogen cooled coldfingers and the Adsorption Trap (AdTrap), an in-line, short GC column packed with Porapak Type-Q$^{TM}$50/80 and silver wool, before being introduced to the mass spectrometer dual inlet. This system operates entirely under vacuum without a carrier gas for the GC column gas separation step. The column is relatively small compared to that on the Autoline and is held at -30°C for the duration of the $CO_2$ transit. The short-length column only allows for use of relatively small samples of mostly pure carbonate. The controlling software, Perspective Stable Gas Control Software, was developed by Nu Instruments.

### 4.1.c *Phosphoric Acid Preparation & Storage*

There are several different recipes used for producing phosphoric acid; here we describe our own laboratory procedures. Acid digestion is facilitated with 105 weight percent (wt%) phosphoric acid ($H_3PO_4$). To achieve this concentration, phosphorus pentoxide ($P_2O_5$) is added to a beaker of 85 wt% phosphoric acid, while continuously stirring on a hotplate set at 300 °C. The $P_2O_5$ reacts with water in the 85 wt% $H_3PO_4$, hydrolyzing the $P_2O_5$ and creating more phosphoric acid. This reaction eliminates the remaining water in the acid and adds phosphoric acid molecules, thus increasing the concentration of phosphoric acid. Concentration of the acid is checked by measuring the density of the acid at room temperature. Our target density is 1.94 to 1.95 g/ml. A ratio of 1.25 kg of phosphorus pentoxide to 1 L of 85% ortho-phosphoric acid produces the desired 105 wt% $H_3PO_4$. This high nominal concentration is achieved due to the polymerization of the phosphate under anhydrous conditions into multimeric acids such as the dimer, pyrophosphoric acid, and the trimer, triphosphoric acid. A density below the target range indicates a still significant proportion of water in the acid, and a need to add more phosphorus pentoxide. A density above the target range indicates an over-concentration with formation of significant amounts of the higher multimers of the acid-phosphate, and is remedied by reduction in hotplate temperature and allowing some water from the atmosphere to be absorbed by the acid. Once at the proper density, the acid is stored in pyrex glass jars inside dehydrated desiccators for future use. Batches immediately to be used for digestion are maintained at 90 °C on a stirring hotplate.

## 4.2 Mass Spectrometers

### 4.2.a *Thermo 253 IRMS*

The Thermo Fisher MAT 253 is the first commercially available high-precision gas-source, sector mass spectrometer that is sufficiently sensitive to be useful for applications of carbonate clumped isotope thermometry (2, 21). The instrument has a dual inlet system and is specifically configured to measure multiply substituted isotopologues of $CO_2$ via an array of Faraday cups capable of simultaneously measuring masses 44, 45, 46, 47, 48, and 49 amu. Detectors for masses 44 through 46 are registered through 3 x$10^8$, 3 x$10^{10}$, and $10^{11}$ Ω resistors, respectively, while detectors for masses 47 through 49 are registered with $10^{12}$ Ω resistors. Electro-polished nickel capillaries are used to deliver sample and reference gas from the bellows to the source instead of the initially outfitted stainless steel capillaries from Thermo Fisher.

Given the low abundance of multiply-substituted isotopologues, relatively large sample sizes and long count times are needed (1, 2, 24). At the beginning of each acquisition, gas pressures in the sample and reference bellows are adjusted to achieve a signal of 16 volts (V) across the mass 44 Faraday cup, resulting in 2-3 V across the mass 47 cup. Each sample of $CO_2$ gas is measured between 7 and 10 gas-working cycles. Data is taken in nine blocks of 10 cycles, with each cycle consisting of 8 seconds of integration and 16 seconds of changeover delay, for a total integration time of 720 seconds per sample. Each block consists of a pressure balance adjustment, peak centering, determination of background, and

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integration time. Measurements range from 16 V to 15.7 V on mass 44 over the course of each block, with a pressure adjustment between blocks to return the beams to 16 V at the start of each block. Typical durations for sample analysis are 2 to 2.5 hours.

### *4.2.b Nu Perspective IS*

The Nu Perspective IRMS is a recent mass spectrometer design featuring secondary electron suppression. The presence of an energy filter fitted in front of the Faraday collector array drives the suppression, and results in a linearity correction that is one to two orders of magnitude less than on the Thermo 253. The detectors for masses 44, 45, and 46 are registered through 3 x$10^8$, 3 x$10^{10}$, and $10^{11}$ Ω resistors, respectively, while the channels for masses 47-49 are registered with $10^{12}$ Ω resistors. Detectors for masses 47-49 are shielded by secondary electron suppressors.

Large samples (> 3 mg pure $CaCO_3$) are measured in bellows mode, with 4 blocks of 20 cycles for a total of 80 cycles of sample-standard comparison with an 8 second changeover delay and 20 seconds of integration per cycle for a total integration time of 1600 seconds. There is continuous pressure adjustment using a Newtonian zeroing technique, with balancing to achieve 16 V (or 80 nA) on mass 44 at every acquisition, rather than only at the beginning of the block.

Small samples (0.25- 0.5 mg pure $CaCO_3$) are measured in microvolume mode, with precisely matched sample and working gas volumes, allowing the gas to deplete at precisely matched rates, and increasing the efficacy of gas usage. The microvolumes allow for a full hour-long measurement to take place on a single sample. Data is taken in three blocks of 20 cycles, with each cycle consisting of 20 seconds of integration and 8 seconds of changeover delay, for a total integration time of 1200 seconds per sample. Measurements range from 80 nA to 30 nA on mass 44 over the course of each sample's acquisition.

## 4.3 Standards

We measured 21 carbonate standards from 4 machine configurations, and analyzed data using two methods. Standards for this study are ones that were measured from 2013 to 2018, and data used for this study are from 2013 through 2018. Our working gas is from Oztech and has a typical $\delta^{13}C$ of -3.6‰ (VPDB) and a typical $\delta^{18}O$ of 25.0‰ (VSMOW). Carbonate standard names and abbreviations are shown in Table 2. With our CABs (Configs. 1-2), we measured equilibrated gas standards, typically daily. We use a 10-standard moving average, with multiple standards typically analyzed each day.

### *4.3.a Equilibrated gas standards*

We utilize four endmember equilibrated gases that differ in their $\delta_{47}$ and $\Delta_{47}$. Gases with two distinct $\delta_{47}$ compositions that differ by ~60‰ are used for the linearity correction. The two gases bracket the $\delta_{47}$ of our Oztech IRMS working gas and our samples. The low $\delta_{47}$ endmember consists of gas drawn from a factory (Airgas) $CO_2$ gas cylinder, equilibrated with 5-10 mL of DI water at 25 °C in a water bath. The enriched $\delta_{47}$ endmember consists of gas produced by acid digestion of a Carrara Marble carbonate standard and 105% phosphoric acid, which is subsequently equilibrated with evaporated DI water in the same bath. Our evaporated DI water is produced by boiling DI water for two days. Water bath equilibrations are done for at least 3 days prior to use, and these gases are referred to as unheated gases. Unheated gases are stored in pyrex or quartz breakseals.

Aliquots of the two unheated gases are equilibrated at a second temperature, 1000 °C, to randomize the distribution of isotopes amongst isotopologues, and theoretically should differ in their $\Delta_{47}$ from the unheated 25 °C equilibrations by 0.9‰ (16, 37). This equilibration is done by heating aliquots of cryogenically purified 25 °C gas that are in quartz breakseals using a muffle furnace that is set to 1000°C for at least two hours, followed by flash cooling to room temperature.

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### *4.3.b Carbonate Standards*

Data for 20 calcite standards and 1 dolomite standard are reported (Table 2). These include ETH-1, ETH-2, ETH-3, ETH-4, IAEA-C1, IAEA-C2, and MERCK as described in Bernasconi et al. (2018), and NBS-19, SRM 88B (dolomite), Mallinckrodt Calcium Carbonate, 102-GC-AZ01, Carmel Chalk, Carrara Marble, CMTile (another homogenized Carrara Marble), Spel 2-8-E, TV01, TV03, and VeinStrom. Carbonate standards obtained from the California Institute of Technology (CIT) and China University of Geosciences (CUG) include 102-GC-AZ01, Carrara Marble, Coral Std. Spel 2-8-E, TV01, TV03, ISTB-1, TB-1, and TB-2. These carbonates span a range of $\delta_{47}$ that is more than 30‰, and about 0.5‰ in $\Delta_{47}$. Raw data and analyzed results are in the Supplement.

## 4.4 Sample-standard bracketing

Typically, 9 analyses are done daily with or using our common acid bath systems, of which 4-5 are standards. Daily runs are often initiated with an equilibrated gas standard, followed by a carbonate standard, 1-2 additional carbonate standards during the run, and end with a carbonate standard. Immediately after machine downtime or maintenance, all analyses conducted are of equilibrated gas and carbonate standards to re-establish reference frames. Analysis of samples is resumed once ~10 standards measured at "expected" values are obtained, to more robustly construct a non-linearity correction with a moving average of 10 standards on either side of a given standard, for a 20-point moving average.

For the Nu Carb sample preparation systems, we solely measure carbonate standards, with 14-15 analyses per day, of which 5-6 are standards. Daily sequences are initiated with two carbonate standards, 1-2 additional carbonate standards during the run, and end with two carbonate standards. Following machine downtime or maintenance, all analyses are of carbonate standards. To ensure a range of standards with different values that should bracket most samples, we cycle through each carbonate standard (see Figure 3 for $\delta_{47}$ and $\Delta_{47}$ ranges). Outliers are excluded at the 3σ level (0.06‰) in $\Delta_{47}$ space (38).

### *4.4.a Corrections*

Over two years, several lab group members entered data from six years of instrumental analyses into Easotope (27). Standardization intervals are primarily identified based on times when the source was cleaned due to a contaminant, the source was retuned, or there were other major changes (for example, a digestion system or GC being repaired). All data are reported using the Brand parameter set (26, 29) on the absolute reference frame (16).

We analyzed data in several ways over multiple years; this study presents the results of two sets of analyses that are most relevant to the community, referred to as analyses B2 and B3. These two analyses differ in the number of standards used for drift corrections and transfer functions, termed "working standards" throughout this study (3 and 8 respectively; see Supplementary Table 2). The remaining standards, processed as unknowns, have been termed "consistency standards".

For analysis B2, $\delta^{13}C$ and $\delta^{18}O$ drift corrections utilize ETH-1, ETH-2, and ETH-3 as working standards. Linearity corrections for all instrument configurations are based on measurements of the carbonate standards ETH-1 and ETH-2 that were produced during heating experiments by the ETHZ group, with values from Bernasconi et al. (2018). For instrument configurations that use a common acid bath system (Configs. 1 and 2), linearity corrections use equilibrated gases in addition to carbonate standards ETH-1 and ETH-2. Transfer functions used for analysis B2 are based on the proposal from the Intercarb exercise (19) to use values from 3 carbonate standards (ETH-1, ETH-2, ETH-3) for corrections; these values are taken from Bernasconi et al. (2018) to evaluate the reproducibility of the remaining carbonate standards (Supplementary Table 2).

For analysis B3, we assess the impact of utilizing a larger number of carbonate standards as working standards for corrections. $\delta^{13}C$ corrections utilize ETH-1, ETH-2, ETH-3, Carmel Chalk, Carrara Marble, CMTile, and VeinStrom; $\delta^{18}O$ drift corrections utilize these and also TV03. Linearity corrections are the same as analysis B2. Transfer functions utilize 8 standards: ETH-1, ETH-2, ETH-3, Carmel Chalk, Carrara Marble, CMTile, VeinStrom, and TV03 (Supplementary Table 2).

## 4.5 Statistical methods

Statistical analyses were performed in R version 4.0.3 (39). To assess whether there were differences in measurements between machines, analyses, or configurations, we created linear mixed effects models for repeated measures in package *nlme* version 3.1-149 (40) followed by adjustment for multiple comparisons and confidence interval estimation in package *emmeans* version 1.5.1 (41). Pooled degrees of freedom are reported from adjustments in *emmeans*; for all models, df = 98 for pairwise comparisons of individual standards by analysis and configuration except where noted, specifically, Carmel chalk in analysis B2 for Config 1, where df = 121. For analysis by configuration comparisons, pooled df = 6992. Several standards (ETH-1, ETH-2, ETH-3, ETH-4) were measured from multiple aliquots of the standard. No differences were found between aliquots, and they were therefore pooled for analyses. Analytical uncertainty was included in models as a random effect in the form of the measurement standard error. Package *emmeans* implements a marginal mean calculation that differs slightly (approx. 0.005‰) from the more typical weighted means approach. However, any discrepancies are within the bounds of calculated uncertainties.

To assess precision, we implemented a linear regression approach using a 75/25 training/test split of observed $\Delta_{47}$ values with prediction post resampling in package *caret* version 6.0-86 (42). Standard TV01 was measured only five times in our dataset, and was excluded from precision analyses due to producing a rank-deficient fit. As findings indicate that there is no measurable difference in standard values between Analysis B2 and B3 (see section 5.4), we chose to consider linear models including standard only as a predictor of $\Delta_{47}$ in addition to standard plus configuration, standard plus analysis, and standard plus configuration and analysis. Rosner's Test for outliers in measurement error was performed in package *EnvStats* version 2.4.0 (43). Data and R code used in analyses are publicly available at https://github.com/Tripati-Lab/Upadhyay-et-al.

# 5. RESULTS AND DISCUSSION

## 5.1 Baselines and linearity corrections

Figure 1 shows baselines for the different instrument configurations. Our Thermo MAT 253 has a larger baseline that gives rise to a linearity correction for $\Delta_{47}$ with a relatively steep slope in the third decimal place (we note this issue should be resolved with the newer generation of Thermo MAT 253+ IRMS). The Nu Perspective IS has lower baselines and relatively flat linearity corrections for $\Delta_{47}$ that vary in the fourth decimal place. This is because the presence of an energy filter and quadratic lenses fitted in front of the faraday collector arrays suppresses secondary electrons, giving rise to an almost negligible linearity correction.

For both types of instruments, we found evidence for baseline stability over timescales of a month or greater. Monitoring of the pressure baseline on each instrument followed a procedure similar to that outlined in Meckler et al., (2014). For the Thermo MAT 253, weekly/monthly scans show a long-term temporal stability between consecutive samples/standards within a correction interval, which are typically one month or longer in length. Weekly peak scans at m/z = 44 intensities ranging from 10 V to 20 V on the MAT 253 yield baselines that ranged from -5 to -40 mV for m/z = 47 (Figure 1). For the Nu Perspective IS, bimonthly peak scans show relative stability typically over a 3 month or longer interval.

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Scans at m/z = 44 intensities ranging from 40 nA to 100 nA (equivalent to 12 V to 30 V) on the Nu Perspectives yield baselines around 0.00005 nA for m/z = 47 (equivalent to 50 mV) (Figure 1).

Figure 2 shows the non-linearity corrections corresponding to the dates of analyses shown in Figs. 1-2. Due to the larger baselines, measurements from the Thermo 253 require a significant linearity slope correction for $\Delta_{47}$ (Figure 2). For the Nu Perspective, there is secondary electron suppression on the m/z = 47 cup which means there should not be a large non-linearity correction for $\Delta_{47}$ (Figure 2).

## 5.2 Use of published values

To report the figures of merit for carbonate-based standardization, we show consistency standard values in Supplementary Tables 3 and 4. Both are on the absolute reference frame and use the Brand parameter set (Brand et al., 2010). Values in Supplementary Table 3 were calculated using ETH-1, ETH-2, and ETH-3 as working standards (Analysis B2), with bulk and clumped isotope values from Bernasconi et al. (2018). For Analysis B3 (Supplementary Table 4), the ETH standards are defined using the Bernasconi et al. (2018) values, and the remaining working standards from analysis B2. Standard values are also recalculated on the absolute reference frame using updated values from Bernasconi et al. (submitted) (Table 2).

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## 5.3 Long-term accuracy & precision of clumped isotope data from multiple instruments

A comparison of standard values shown in Supplementary Tables 3 and 4 was done to assess machine intercomparability and the impact of using different numbers of working standards for reference frame calculations. We analyzed these results to examine whether there are differences in the accuracy and precision of clumped isotope data arising from acid digestion, mass spectrometer, the number of working standards used, and the use of equilibrated gases for reference frame calculations. To assess accuracy, we compare standard $\Delta_{47}$ values to those from the Nu Perspective IS with a 90°C common acid bath (Config. 2). We assume this to be the most accurate of the configurations investigated for three reasons:

(1) a relatively small linearity correction for $\Delta_{47}$;
(2) the use of equilibrated gas standards in addition to carbonate standards allowing for values to be directly tied to the absolute reference frame which is based on the $CO_2$ equilibrium scale (CDES)$^{(16)}$, and provides an additional check on the origin of drift;
(3) larger samples are analyzed that should minimize the impact of any heterogeneity in measured materials;
(4) larger samples facilitate longer counting times with stable and intense voltages.

Standard $\Delta_{47}$ values are presented in Supplementary Tables 3 and 4 (Figure 4 & Supplementary Figure 1 provides a visual representation of data presented in these tables). To assess precision, we considered models for $\Delta_{47}$ which comprised standard alone, the additive effects of standard plus configuration, the additive effects of standard plus analysis, and the additive effects of standard plus configuration and analysis. We achieved better than 98% precision in all cases, with root mean square errors (RMSE) of 0.025 and mean absolute errors (MAE) of 0.019 regardless of the combination of factors. For full model output from each comparison, see Supplementary Table 5).

The results for these investigations reveal that differences in precision between acid digestion systems and mass spectrometers are less than 2% (absolute value 0.02‰). We also find there is not a major improvement in accuracy through the use of carbonate standards relative to mixed gas-and-carbonate standardization for the non-linearity correction, or if 3 or 8 standards are used for drift corrections and the construction of transfer functions, assuming multiple standards are run each day. Mean percent error across all $\Delta_{47}$ measurements in this study is 0.03% (median = 0%), ranges from -

38.7% to 29.2%, and is normally distributed. However, the nine most extreme errors are true outliers (Rosner's Test, k = 10; see Supplementary Table 6 for full output, Figure 5 for histograms of errors, and Supplementary Table 7 for errors by standard, configuration, and analysis). Following removal of outliers, errors have a mean of 0.06% and median of 0%, with a range from -27.6% to 27.8%, and are normally distributed.

## 5.4 Comparison of mean values across machine configurations using 3 vs 8 standards with analyses B2 and B3 for Nu Perspective IS with CAB

Comparison of analyses B2 and B3 allow us to investigate the effect of using a larger number of working standards with the common acid bath (CAB) system paired with the Nu Perspective IS (Config. 2), the instrumental configuration that we assume is the most robust given the large standard sizes which minimize the potential impact of heterogeneity, secondary electron suppression, long integration times, and intense ion beams. Both analyses use ETH-1, ETH-2, and ETH-3 as working standards. In addition, we use values of 5 consistency standards determined during analysis B2 (Carmel Chalk, Carrara Marble, CMTile, TV03, and Veinstrom) to bootstrap the values used for working standards in B3.

Mean $\Delta_{47}$ values are within error of each other for all instrumental configurations, and the number of standards used for drift and transfer function corrections makes a negligible difference in both the mean and the reproducibility of clumped data. Consistency standard ETH-4 yields a mean $\Delta_{47}$ value of 0.518±0.017 (95% CI: 0.508 - 0.518) on Config. 2 in Analysis B2 (n = 69) and a mean value of 0.519±0.017 (95% CI: 0.508 - 0.518) on Config. 2 in Analysis B3 (n = 66), yielding a 0.001‰ difference in $\Delta_{47}$ values (Supplementary Tables 3, 4, and 8). Consistency standard SRM 88B yields a mean $\Delta_{47}$ value of 0.577±0.005 (95% CI: 0.578 - 0.596) on Config. 2 in Analysis B2 (n = 10) and a mean value of 0.573±0.007 (95% CI: 0.578 - 0.596) on Config. 2 in Analysis B3 (n = 10), with a 0.004‰ difference in $\Delta_{47}$ values (Supplementary Tables 3, 4, and 8). We find no evidence of a statistically significant difference between the two analyses for either standard (Both analyses: Estimate = -0.0002, SE = 0.003, t ratio = -0.062, p = 1). To see full summary statistics and confidence intervals produced by *emmeans*(41) for each standard across all instruments and configurations, see Supplementary Table 8.

## 5.5 Comparison of mean values across machine configurations in analysis B2

For Analysis B2, we examine the impact that acid digestion system, mass spectrometer model, and the use of a mixed-gas-and-carbonate standardization scheme have on the reproducibility of consistency standards.

### *5.5.a No evidence for differences in accuracy and precision between acid digestion systems, acid temperatures, or small vs. large samples*

We first assess the effect of acid digestion procedure, acid temperature, and sample size by comparing results from the 90 °C common acid bath (CAB) system (Config. 2) with large samples, to the 70 °C Nu Carb system (Config. 3A) with small samples. These configurations both utilize the same mass spectrometer model (Nu Perspective), but differ in the use of gas-and-carbonate-based standardization vs carbonate-based standardization for the non-linearity correction (Table 1). The comparison demonstrates that acid digestion systems, acid temperatures, and sample size negligibly affects the reproducibility of clumped data. The low values for absolute difference from 'true' $\Delta_{47}$ values in these cases demonstrate that both acid digestion systems yield similarly accurate and precise data with sufficient replication (Figure 6, Supplementary Table 3, and Supplementary Figure 1). For example, Carmel Chalk yields a mean $\Delta_{47}$ value of 0.665±0.018 (95% CI: 0.660 - 0.670) on Config. 2 (n = 95) and a mean value of 0.658±0.022 (95% CI: 0.659 - 0.670) on Config. 3A (n = 33), with a 0.007‰ difference in $\Delta_{47}$ values.

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ETH-4 yields a mean $\Delta_{47}$ value of 0.518±0.017 (95% CI: 0.508 - 0.518) on Config. 2 (n = 69) and a mean value of 0.513±0.022 (95% CI: 0.507 - 0.517) on Config. 3A (n = 23), with a 0.005‰ difference in $\Delta_{47}$ values. After adjustment for multiple comparisons, we find no evidence of a difference between Configs. 2 and 3A in Analysis B2 (Estimate = 0.0006, SE = 0.003, t ratio =0.205, p = 1) across all measured standards.

Similar results are obtained when we compare Config. 2 with Config. 3B (which is the same configuration as 3A). Once again, we find no evidence of a statistically significant difference between configurations (Estimate = -0.003, SE = 0.003, t-ratio = -1.270, p = 0.9). This suggests that both machine configurations yield similarly accurate and precise data (Supplementary Table 3). Carmel Chalk yields a mean $\Delta_{47}$ value of 0.665±0.018 (95% CI: 0.659 - 0.670) on Config. 2 (n = 95) and a mean value of 0.664±0.024 (95% CI: 0.664 - 0.673) on Config. 3B (n = 129), with a 0.001‰ difference in $\Delta_{47}$ values. ETH-4 yields a mean $\Delta_{47}$ value of 0.518±0.017 (95% CI: 0.508 - 0.518) on Config. 2 (n = 69) and a mean value of 0.516±0.021 (95% CI: 0.511 - 0.521) on Config. 3B (n = 23), with a 0.002‰ difference in $\Delta_{47}$ values.

### *5.5.b No evidence for improved accuracy using the Nu Perspective vs. Thermo 253 with the 3 standard correction*

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To determine the effect of mass spectrometer model, we compare results for consistency standards between Config. 1 (Thermo 253) with Configs. 2 (Nu Perspective). We also conduct a comparison of consistency standards between Configs. 1 and 3B (the Thermo 253 and second Nu Perspective used in this study, respectively). In these comparisons, we find a slight improvement in accuracy of the Nu Perspective over the Thermo 253, which may be due to the limitations of not having a sufficient number of standards to characterize instrument drift on the Thermo 253, but no improvement in precision.

We observe no significant difference in $\Delta_{47}$ values between Config. 1 (Thermo 253) and Config. 2 (Nu Perspective) (Estimate = -0.006, SE = 0.003, t-ratio = -2.326, p = 0.3) (Figure 6). Carmel Chalk yields a mean $\Delta_{47}$ value of 0.665±0.018 (95% CI: 0.660 - 0.670) on Config. 2 (n = 95) and a mean value of 0.662±0.021 (95% CI: 0.654 - 0.664) on Config. 1 (n = 68), with a 0.003‰ difference in $\Delta_{47}$ values. ETH-4 yields a mean $\Delta_{47}$ value of 0.518±0.017 (95% CI: 0.508 - 0.518) on Config. 2 (n = 69) and a mean value of 0.499±0.021 (95% CI: 0.502 - 0.512) on Config. 1 (n = 69), with a 0.019‰ difference in $\Delta_{47}$ values. Measured values are not significantly different between these mass spectrometer models when adjusted for multiple comparisons.

We observe a significant difference in $\Delta_{47}$ values between Configs. 1 and 3B (the Thermo 253 and Nu Perspective) (Estimate = -0.009, SE = 0.002, t-ratio = -3.741, p = 0.007) at the instrument level (See standards ETH-4 and TV03 in Figure 6). Carmel Chalk yields a mean $\Delta_{47}$ value of 0.662±0.021 (95% CI: 0.654 - 0.664) on Config. 1 (n = 68) and a mean value of 0.664±0.024 (95% CI: 0.664 - 0.673) on Config. 3B (n = 129), yielding a 0.001‰ difference in $\Delta_{47}$ values. ETH-4 yields a mean $\Delta_{47}$ value of 0.499±0.021 (95% CI: 0.502 - 0.512) on Config. 1 (n = 68) and a mean value of 0.516±0.021 (95% CI: 0.511 - 0.521) on Config. 3B (n = 82), with a 0.017‰ difference in $\Delta_{47}$ values. TV03 yields a mean $\Delta_{47}$ value of 0.687±0.026 (95% CI: 0.695 - 0.707) on Config. 1 (n = 35) and a mean value of 0.770±0.030 (95% CI: 0.704 - 0.716) on Config. 3B (n = 15), with a 0.083‰ difference in $\Delta_{47}$ values. However, when standards are examined on a pairwise basis, this difference is eliminated by adjustment for multiple comparisons (Estimate = -0.009, SE = 0.002, t-ratio = -3.741, p = 0.5 for all standards).

## 5.6 Comparison of mean values across machine configurations in analysis B3

### *5.6.a No evidence for differences in accuracy and precision between acid digestion systems or acid temperatures on the Nu*

Comparison of Config. 2 (Nu Perspective + 90°C common acid bath) and Config. 3A (Nu Perspective + 70°C Nu Carb) (Supplementary Table 4) yields results that are similar to analysis B2, . ETH-4 yields a mean $\Delta_{47}$ value of 0.519±0.017 (95% CI: 0.508 - 0.518) on the Nu Perspective IS (Config. 2; n = 66) and a mean value of 0.518±0.025 (95% CI: 0.508 - 0.517) on the Nu Perspective IS (Config. 3A; n = 36), with a 0.001‰ difference in $\Delta_{47}$ values (Figure 6). We find no evidence of a statistically significant difference between the configurations (Estimate = 0.0004, SE = 0.003, t-ratio = 0.167, p = 1). Results are similar to those obtained from analysis B2, with low deviation from 'true' $\Delta_{47}$ values and low variability in standard deviations suggesting that acid digestion system, acid temperature, and sample size do not affect reproducibility.

The same comparison was done with Config. 2 and Config. 3B (a second Nu Perspective + 70°C Nu Carb). Results are similar to those obtained from the above comparison, and to analysis B2. Once again, the low absolute difference from 'true' $\Delta_{47}$ values demonstrate that both machine configurations yield similarly accurate and precise data (Figures 4, 6, and Supplementary Table 4). We find no evidence of a statistically significant difference (Estimate = 0.0003, SE = 0.002, t-ratio = 0.119, p = 1). ETH-4 yields a mean $\Delta_{47}$ value of 0.519±0.017 (95% CI: 0.508 - 0.518) on Config. 2 (n = 66) and a mean value of 0.510±0.021 (95% CI: 0.508 - 0.518) on Config. 3B (n = 131), with a 0.009‰ difference in $\Delta_{47}$ values.

### *5.6.b No evidence for improved accuracy using the Nu Perspective vs. Thermo 253*

Comparison of Config. 1 (Thermo 253 + CAB) to Config. 2 (NuPerspective + CAB) and Config. 3B (NuPerspective + Nu Carb) shows shows there is no statistically significant difference between mass spectrometer models (Config. 1 vs 2: Estimate = -0.002, SE = 0.002, t-ratio = -0.692, p = 1; Config. 1 vs 3B: Estimate: -0.005, SE = 0.002, t-ratio = -2.108, p = 0.4; Config. 2 vs. 3B: Estimate = 0.0003, SE = 0.002, t-ratio = 0.119, p = 1) (Figure 6). ETH-4 yields a mean $\Delta_{47}$ value of 0.519±0.017 (95% CI: 0.508 - 0.518) on Config. 2 (n = 66) and a mean value of 0.510±0.020 (95% CI: 0.507 - 0.516) on Config. 1 (n = 128), with a 0.009‰ difference in $\Delta_{47}$ values. SRM 88B yields a mean $\Delta_{47}$ value of 0.573±0.007 (95% CI: 0.578 - 0.596) on Config. 2 (n = 10) and a mean value of 0.595±0.026 (95% CI: 0.577 - 0.595) on the Config. 1 (n = 8), with a 0.025‰ difference in $\Delta_{47}$ values. ETH-4 yields a mean $\Delta_{47}$ value of 0.510±0.020 (95% CI: 0.507 - 0.516) on Config. 1 (n = 128) and a mean value of 0.510±0.021 (95% CI: 0.508 - 0.517) on the Config. 3B (n = 131), yielding a 0.000‰ difference in $\Delta_{47}$ values. IAEA-C1 yields a mean $\Delta_{47}$ value of 0.347±0.024 (95% CI: 0.352 - 0.365) on Config. 1 (n = 17) and a mean value of 0.362±0.028 (95% CI: 0.353 - 0.366) on Config. 3B (n = 34), with a 0.015‰ difference in $\Delta_{47}$ values.

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## 5.7 No evidence for improved reproducibility via implementation of carbonate-based standardization vs gas-and-carbonate-based standardization

The Nu Carb systems used in Configs. 3A and 3B utilize carbonates for the non-linearity correction, while the common acid bath systems used in Configs. 1 and 2 use carbonates in conjunction with equilibrated gases to construct the non-linearity correction. A comparison of values across digestion systems indicate that there may not be a direct benefit in incorporating equilibrated gases in the non-linearity correction (Figure 6, Supplementary Tables 3 & 4).

For Analysis B2, we measure the effect of utilizing equilibrated gases by first comparing results from Config. 2 (gas-and-carbonate-based standardization) with those from Configs. 3A and 3B (carbonate-based standardization) (Figure 6, Supplementary Table 3). Carmel Chalk yields a mean $\Delta_{47}$ value of 0.665±0.018 (95% CI: 0.660 - 0.670) on Config. 2 (n = 95), a mean value of 0.658±0.022 (95% CI: 0.659- 0.670) on Config. 3A (n = 33), and a mean value of 0.664±0.024 (95% CI: 0.664 - 0.673) on Config. 3B (n=129). This yields a 0.003‰ difference in $\Delta_{47}$ values between Configs. 2 and 3A, and a 0.001‰ difference in $\Delta_{47}$ values between Configs. 2 and 3B. ETH-4 yields a mean $\Delta_{47}$ value of 0.518±0.017 (95% CI: 0.508 - 0.518) on Config. 2 (n = 69), a mean value of 0.513±0.022 (95% CI: 0.507 - 0.517) on Config. 3A (n = 23), and a mean value of 0.516±0.021 (95% CI: 0.511 - 0.521) on Config. 3B (n = 82). This yields a 0.005‰ difference in $\Delta_{47}$ values between Configs. 2 and 3A, and a 0.002‰ difference in $\Delta_{47}$ values between Configs. 2 and 3B. We find no evidence that any of these differences are statistically significant (Config. 2 vs 3A: Estimate = 0.0006, SE = 0.003, t-ratio = 0.205, p = 1; Config 2 vs 3B: Estimate = -0.003, SE = 0.003, t-ratio = -1.270, p = 0.9).

We also compare Analysis B2's results from Config. 1 (gas-and-carbonate-based standardization) with those from Configs. 3A and 3B (carbonate-based standardization) (Figure 6, Supplementary Table 3). Carmel Chalk yields a mean $\Delta_{47}$ value of 0.662±0.021 (95% CI: 0.654 - 0.664) on Config. 1 (n = 86), a mean value of 0.658±0.022 (95% CI: 0.659 - 0.670) on Config. 3A (n = 33), and a mean value of 0.664±0.024 (95% CI: 0.664 - 0.673) on Config. 3B (n=129). This yields a 0.004‰ difference in $\Delta_{47}$ values between Configs. 1 and 3A, and a 0.002‰ difference in $\Delta_{47}$ values between Configs. 1 and 3B. ETH-4 yields a mean $\Delta_{47}$ value of 0.499±0.021 (95% CI: 0.502 - 0.512) on Config. 1 (n = 69), a mean value of 0.513±0.022 (95% CI: 0.507 - 0.517) on Config. 3A (n = 23), and a mean value of 0.516±0.021 (95% CI: 0.511 - 0.521) on Config. 3B (n = 82). This yields a 0.014‰ difference in $\Delta_{47}$ values between Configs. 1 and 3A, and a 0.017‰ difference in $\Delta_{47}$ values between Configs. 1 and 3B. For Analysis B2, there is no improved accuracy or precision in the use of a carbonate-based vs. gas-and-carbonate-based standardization, given that there are no statistically significant differences between them (Config. 1 vs 3A: Estimate = -0.005, SE = 0.003, t-ratio = -1.950, p = 0.5; as above the difference between Config. 1 vs. 3B [Estimate = -0.009, SE = 0.002, t-ratio = -3.741, p = 0.007] is no longer significant at the standard level after adjustment for multiple comparisons [Estimate = -0.009, SE = 0.002, t-ratio = -3.741, p = 0.5 for all standards]).

For Analysis B3, we follow the same approach and first compare data from Config. 2 (gas-and-carbonate-based standardization) with those from Configs. 3A and 3B (carbonate-based standardization) (Figure 6, Supplementary Table 4). ETH-4 yields a mean $\Delta_{47}$ value of 0.519±0.017 on Config. 2 (n = 66), a mean value of 0.518±0.025 on Config. 3A (n = 36), and a mean value of 0.510±0.021 on Config. 3B (n=131). This yields a 0.001‰ difference in $\Delta_{47}$ values between Configs. 2 and 3A, and a 0.009‰ difference in $\Delta_{47}$ values between Configs. 2 and 3B. These data show no significant differences in accuracy or precision by use of a mixed gas-and-carbonate-based standardization approach (Config. 2 vs 3A: Estimate = 0.0004, SE = 0.003, t-ratio = 0.167, p = 1; Config. 2 vs 3B: Estimate = 0.0003, SE = 0.002, t-ratio = 0.119, p = 1).

We also compare Analysis B3's results from Config. 1 (carbonate + equilibrated gas standardization) with those from Configs. 3A and 3B (carbonate-based standardization) (Figure 6, Supplementary Table 4). ETH-4 yields a mean $\Delta_{47}$ value of 0.510±0.020 (95% CI: 0.507 - 0.516) on Config. 1 (n = 128), a mean value of 0.518±0.025 (95% CI: 0.508 - 0.517) on Config. 3A (n = 36), and a mean value of 0.510±0.021 (95% CI: 0.508 - 0.517) on Config. 3B (n=131). This yields a 0.008‰ difference in $\Delta_{47}$ values between Configs. 1 and 3A, and a 0.000‰ difference in $\Delta_{47}$ values between Configs. 1 and 3B. IAEA-C1 yields a mean $\Delta_{47}$ value of 0.347±0.024 (95% CI: 0.352 - 0.365) on Config. 1 (n = 17), a mean value of 0.365±0.020 (95% CI: 0.353 - 0.367) on Config. 3A (n = 17), and a mean value of 0.362±0.028 (95% CI: 0.353 - 0.366) on Config. 3B (n = 34). This yields a 0.018‰ difference in $\Delta_{47}$ values between Configs. 1 and 3A, and a 0.015‰ difference in $\Delta_{47}$ values between Configs. 1 and 3B. Data for additional consistency standards are given below, with no standards showing a significant difference across configurations (Config. 1 vs 3A: Estimate = -0.001, SE = 0.002, t-ratio =-0.482, p = 1; Config. 1 vs 3B: Estimate: -0.005, SE = 0.002, t-ratio = -2.108, p = 0.4).

Thus, for all consistency standards measured across these configurations in Analyses B2 and B3, the absolute differences in $\Delta_{47}$ values are minimal, consistently under 0.02‰. Considering analyses across all standards and configurations, there is no evidence of a difference between Analyses B2 and B3 (Estimate = -0.0004, SE = 0.001, pooled df = 6992, t-ratio = -0.350, p = 0.7). We see no improved or reduced accuracy or precision due to the use of carbonate-based standardization vs. implementation of a mixed-gas-and-carbonate-based standardization scheme using these methods.

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## 5.8 Comparison of long-term precision

Long-term precision was determined by comparing analyses from *emmeans* (i.e., Standard alone, Standard plus Configuration, Standard plus Analysis, and Standard plus Configuration and Analysis). All comparisons yielded RMSE=0.025 and MAE=0.019 (Supplementary Table 5), with differences in precision between acid digestion systems and mass spectrometers being less than 2% (absolute value 0.02‰). Mean error across all $\Delta_{47}$ measurements is 0.03% (median = 0%), ranges from -38.7% to 29.2%, and is normally distributed. Nine outliers were determined via a Rosner's Test (k=10; see Figure 5 and Supplementary Tables 6 & 7). Once outliers are removed, mean error is 0.06% and median error is 0%. Errors range from -27.6% to 27.8%, and are normally distributed.

Figure 7 and Supplementary Figure 2 show standard residuals as a function of analysis date for each instrumental configuration, for Analyses B3 and B2, respectively. Figure 4 and Supplementary Figure 1 shows $\Delta_{47}$ residuals and their standard deviation for each machine configuration in both Analyses. In each of the above figures, with the exception of data obtained for TV03 on Config. 1 in Analysis B2, all configurations and standards yield extremely similar results for $\Delta_{47}$ residual and $\Delta_{47}$ residual standard deviation. A normality test for the residuals, using those from Config. 2 as "true" values, shows the distribution of residuals are indistinguishable from a normal distribution. Supplementary Figure 3 shows that all instrument configurations approach shot noise limits after 3-20 replicates, depending on beam intensity and integration time.

## 6. RECOMMENDATIONS

These results show it is possible to obtain comparable data for different mass spectrometers, using methods described in this study and references therein. We recommend a high frequency of standard analyses, with 3-5 standards run in a day for the instrumental configurations described here, as this allows for the adequate characterization of the behavior of each instrument that can occur on short time frames. Typically, for all instrumental configurations, a 20-point moving average was sufficient to characterize instrument drift (with 10 points on either side of a given working standard).

Related to this, a significant step in obtaining reproducible results on one instrument through time, and comparable results between different types of instrumentation, is the determination of standardization windows (aka correction intervals). Here these are defined based on either major instrument upkeep events (e.g., source retuning) or phenomenological changes in raw data. A previous study (18) showed that use of 1-month standardization windows on these instrumental configurations yields comparable results between instruments.

We recommend using at least two standards (gas and/or carbonates) with a stochastic distribution to construct the non-linearity correction, as previously suggested (1, 16, 17). Our analyses show that use of either equilibrated gases or carbonates, or of a mixed gas/carbonate standardization, does not make a statistically significant difference in results. This implies it is feasible to eliminate the use of equilibrated gases. However, we note that for diagnostic purposes, we continue to run equilibrated gases for our common acid bath systems, as this allows us to assess whether the consistent drift or shift in values arises from the carbonate digestion and purification system or mass spectrometer.

For transfer functions, the use of 3 standards that span a range of $\delta_{47}$ and $\Delta_{47}$ space, such as ETH-1, ETH-2, and ETH-3, yields similar results to using 8 standards, if multiple standards are measured each day, We also recommend using multiple ancillary standards as a consistency check. If a sufficient number of standards are used, similarly accurate and precise data should be achievable on different types of instrumentation irrespective of (1) the size of baselines, (2) the slopes of the non-linearity corrections, (3) the number of working standards used (as long as n>3 and appropriately constrains the non-linearity correction and ETF), or (4) whether a carbonate-based or gas-and-carbonate-based standardization procedure is used. We found with a range of instruments and digestion systems that standards yield

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similar mean values, and that a long-term reproducibility of 0.02‰, or a precision of 98.2%, was achievable.

## 7. CONCLUSIONS

This study progresses our understanding of practices that contribute to the intercomparability of $\Delta_{47}$ measurements from different acid digestion systems and mass spectrometer models. We report the long-term accuracy and reproducibility of consistency standards measured on different configurations, using either a mix of equilibrated gas standards and heated carbonate standards to determine the non-linearity correction, or carbonate standards on their own. We also examine the use of 3 or 8 carbonate standards for drift corrections and the construction of transfer functions, using a 20-point moving average, and report the isotopic compositions of 21 different standards.

We show that when instrument behavior is well characterized, negligible differences in reproducibility stem from the acid digestion system used, the mass spectrometer model used, the use of 3 or 8 carbonate standards (with at least two having a stochastic distribution and varying in $\delta_{47}$, and two varying in $\Delta_{47}$), or the use of stochastic carbonate standards or equilibrated gases in the non-linearity correction. The common acid bath system and small sample Nu Carb system yield similar results. Depending on instrument configuration, counting times, sample size and sample heterogeneity, it should be possible to obtain close to shot noise on all instrument configurations.

We report values for 21 different standards on the absolute reference frame using the Brand parameter set (29), including from UCLA, ETHZ, Caltech, and China University of Geosciences. The demonstration of inter-comparability between different instrumental configurations in concert with these standard values supports the generation of datasets that will be intercomparable between a diversity of laboratories using different generations of instrumentation. It also facilitates a restandardization of published data going back to the first carbonate clumped isotope measurements in 2006, on the absolute reference frame, so they can be compared to recently generated data and be intercomparable.

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## 8. ACKNOWLEDGEMENTS

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# Figure captions

**Figure 1**. PBL variations over the course of 2014-2017 on Configuration 1 (Thermo 253) and Configuration 2 (Nu Perspective). Negative values are indicated by grey shading. On the left is an expanded view of the lowermost section of the m/z 44-49 peaks, with m/z 44 at 16 V. On the right, m/z 47 is shown, with m/z 44 voltage corresponding to 10, 12, 14, 16, 18, and 20 V for Configuration 1, and m/z 44 voltage corresponding to 40, 80, and 100 nA for Configuration 2. (A) & (B) Configuration 1 on 10/4/2014, (C) & (D) Configuration 1 on 8/1/2017, (E) & (F) Configuration 2 on 10/12/2015, and (G) & (H) Configuration 2 on 1/18/2016.

**Figure 2**. $\Delta_{47}$ and $\Delta_{48}$ nonlinearity corrections corresponding to the dates of peak scans conducted in Fig. 1, for Configuration 1 (Thermo 253) and Configuration 2 (Nu Perspective). Correction dates are: (A) Configuration 1 $\Delta_{47}$ nonlinearity from 10/4/2014, (B) Configuration 1 $\Delta_{48}$ nonlinearity from 10/4/2014, (C) Configuration 1 $\Delta_{47}$ nonlinearity from 8/1/2017, (D) Configuration 1 $\Delta_{48}$ nonlinearity from 8/1/2017, (E) Configuration 2 $\Delta_{47}$ nonlinearity from 10/12/2015, (F) Configuration 2 $\Delta_{48}$ nonlinearity from 10/12/2015, (G) Configuration 2 $\Delta_{47}$ nonlinearity from 1/18/2016, and (H) Configuration 2 $\Delta_{48}$ nonlinearity from 1/18/2016.

**Figure 3**. Mean $\Delta_{47}$ (‰; CDES) and standard error vs. $\delta_{47}$ (‰; WG) for 21 standards (filled symbols = working standards; open symbols = consistency standards; circles = UCLA standards; squares = CIT or CUG standards). (A) Analysis B2, (B) Analysis B3.

**Figure 4**. Mean standard $\Delta_{47}$ CDES and residuals for each instrumental configuration determined from Analysis B3. (A) Mean standard $\Delta_{47}$ and standard deviation (bold = working standards; italics = CIT or CUG standards; n is indicated next to each standard). Also shown is the average $\Delta_{47}$ from all configurations (black star). (B) Unweighted $\Delta_{47}$ residuals and standard deviations.

**Figure 5.** Histograms of percent error in $\Delta_{47}$ measurements. (A) Before removal of outliers. (B) After removal of outliers (See main manuscript Section 5.3 and Supplementary Information Tables 6 and 7). Solid vertical lines indicate the mean percent error and dotted vertical lines indicate the first and third quarters. Median error for both A and B is 0%.

**Figure 6.** Comparison of mean $\Delta_{47}$ values (‰; CDES) for consistency standards determined on four different instrumental configurations. Also shown is a 1:1 line. Left panels have Configuration 2 as the x-axis; Right panels have Configuration 1 as the x-axis. (A) and (C) Analysis B2. (B) and (D) Analysis B3. All but one standard yielded statistically indistinguishable values in Analysis B2; all standards yielded statistically indistinguishable values in Analysis B3.

**Figure 7**. Individual standard $\Delta_{47}$ residuals for each measurement for each instrumental configuration over multiple years for Analysis B3, after Meckler et al. (2014). Each symbol represents a residual calculated from a single analysis relative to mean values from Supplementary Table 4, and the error bar represents 1 standard error. Vertical dotted gray lines indicate the boundaries of each correction interval. Horizontal dark gray band indicates a standard deviation of 1σ from the mean, intermediate gray indicates a standard deviation of 2σ from the mean, and light gray band indicates a standard deviation of 3σ from the mean. (A) Configuration 1, (B) Configuration 2, (C) Configuration 3A, and (D) Configuration 3B.

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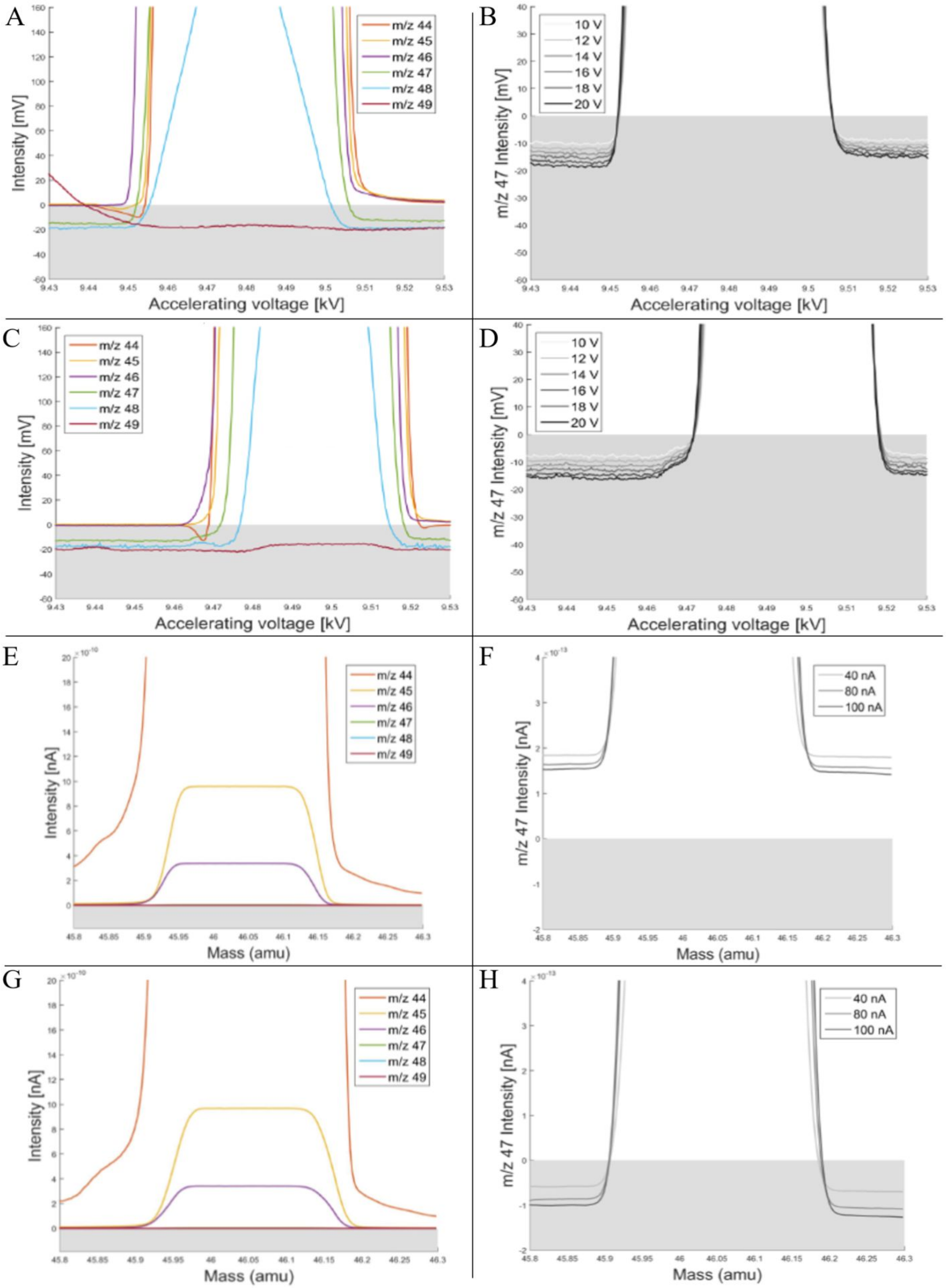
A
Intensity [mV]
Accelerating voltage [kV]
m/z 44
m/z 45
m/z 46
m/z 47
m/z 48
m/z 49
B
m/z 47 Intensity [mV]
Accelerating voltage [kV]
10 V
12 V
14 V
16 V
18 V
20 V
C
Intensity [mV]
Accelerating voltage [kV]
m/z 44
m/z 45
m/z 46
m/z 47
m/z 48
m/z 49
D
m/z 47 Intensity [mV]
Accelerating voltage [kV]
10 V
12 V
14 V
16 V
18 V
20 V
E
Intensity [nA]
Mass (amu)
×10⁻¹⁰
m/z 44
m/z 45
m/z 46
m/z 47
m/z 48
m/z 49
F
m/z 47 Intensity [nA]
Mass (amu)
×10⁻¹³
40 nA
80 nA
100 nA
G
Intensity [nA]
Mass (amu)
×10⁻¹⁰
m/z 44
m/z 45
m/z 46
m/z 47
m/z 48
m/z 49
H
m/z 47 Intensity [nA]
Mass (amu)
×10⁻¹³
40 nA
80 nA
100 nA

**Figure 1**

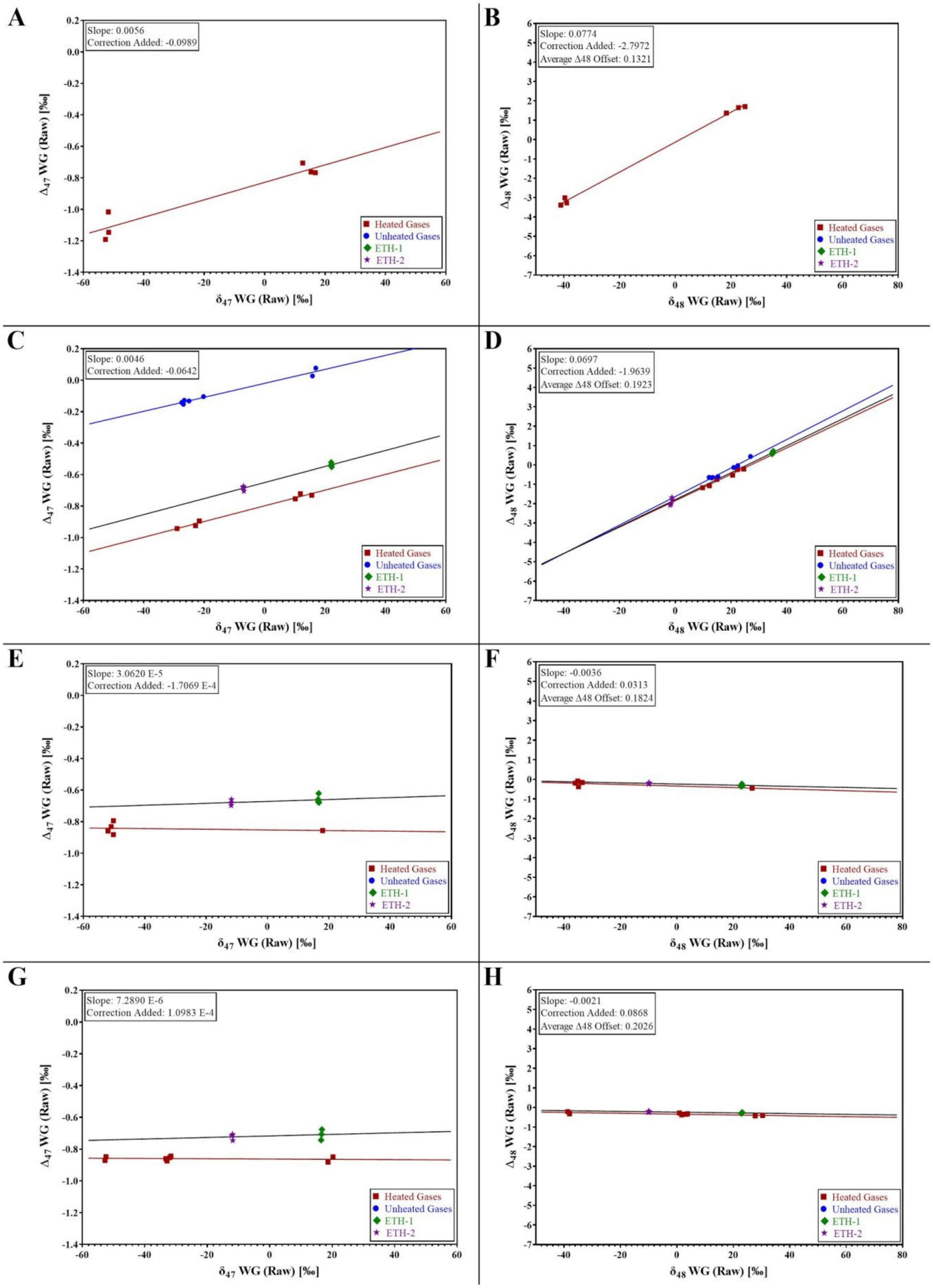
A
Slope: 0.0056
Correction Added: -0.0989
Δ47 WG (Raw) [‰]
δ47 WG (Raw) [‰]
B
Slope: 0.0774
Correction Added: -2.7972
Average Δ48 Offset: 0.1321
Δ48 WG (Raw) [‰]
δ48 WG (Raw) [‰]
C
Slope: 0.0046
Correction Added: -0.0642
D
Slope: 0.0697
Correction Added: -1.9639
Average Δ48 Offset: 0.1923
E
Slope: 3.0620 E-5
Correction Added: -1.7069 E-4
F
Slope: -0.0036
Correction Added: 0.0313
Average Δ48 Offset: 0.1824
G
Slope: 7.2890 E-6
Correction Added: 1.0983 E-4
H
Slope: -0.0021
Correction Added: 0.0868
Average Δ48 Offset: 0.2026
Heated Gases
Unheated Gases
ETH-1
ETH-2

Figure 2

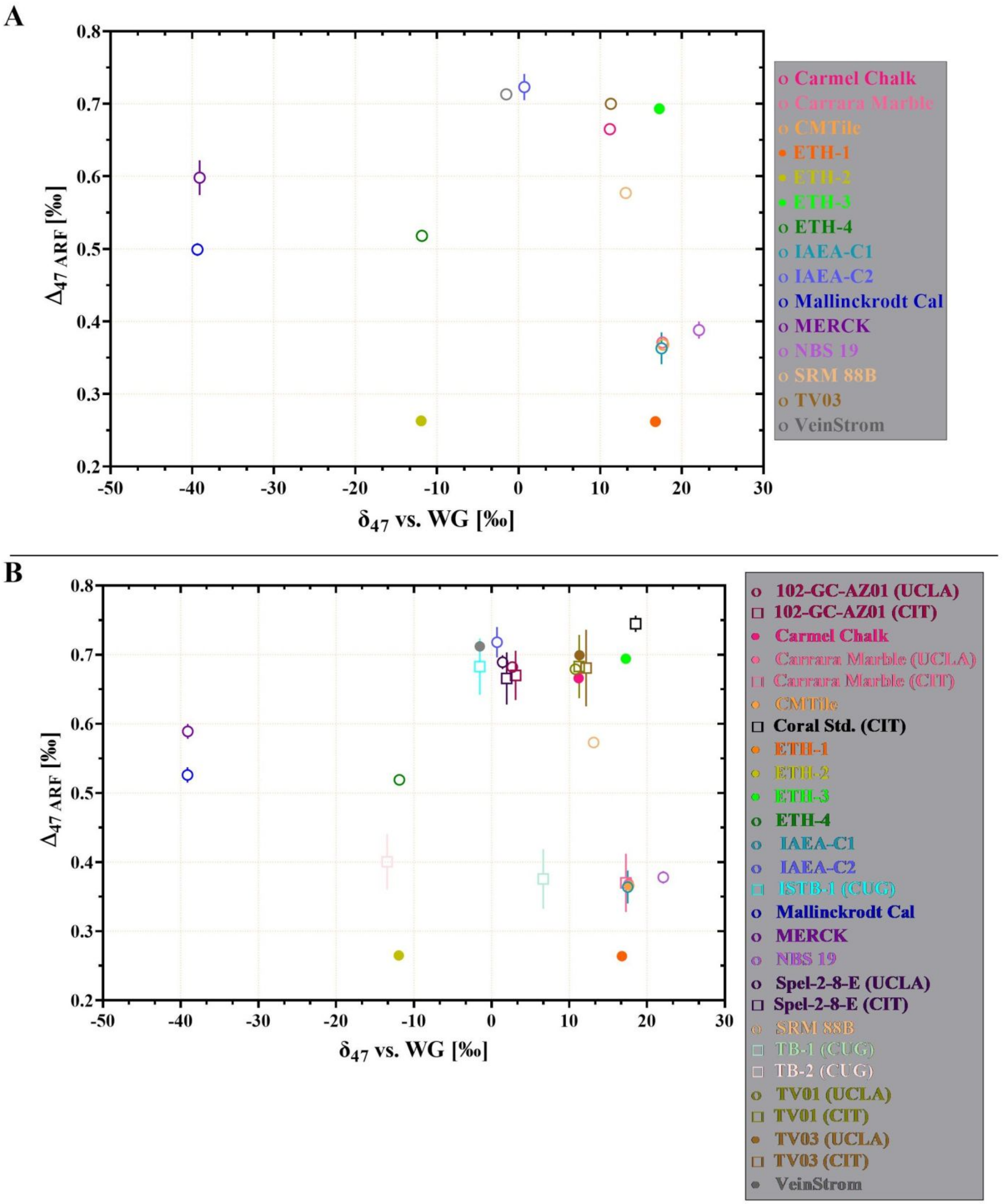
A
$\Delta_{47\ ARF}$ [‰]
$\delta_{47}$ vs. WG [‰]
0.2
0.3
0.4
0.5
0.6
0.7
0.8
-50
-40
-30
-20
-10
0
10
20
30
Carmel Chalk
Carrara Marble
CMTile
ETH-1
ETH-2
ETH-3
ETH-4
IAEA-C1
IAEA-C2
Mallinckrodt Cal
MERCK
NBS 19
SRM 88B
TV03
VeinStrom
B
$\Delta_{47\ ARF}$ [‰]
$\delta_{47}$ vs. WG [‰]
0.2
0.3
0.4
0.5
0.6
0.7
0.8
-50
-40
-30
-20
-10
0
10
20
30
102-GC-AZ01 (UCLA)
102-GC-AZ01 (CIT)
Carmel Chalk
Carrara Marble (UCLA)
Carrara Marble (CIT)
CMTile
Coral Std. (CIT)
ETH-1
ETH-2
ETH-3
ETH-4
IAEA-C1
IAEA-C2
ISTB-1 (CUG)
Mallinckrodt Cal
MERCK
NBS 19
Spel-2-8-E (UCLA)
Spel-2-8-E (CIT)
SRM 88B
TB-1 (CUG)
TB-2 (CUG)
TV01 (UCLA)
TV01 (CIT)
TV03 (UCLA)
TV03 (CIT)
VeinStrom

**Figure 3**

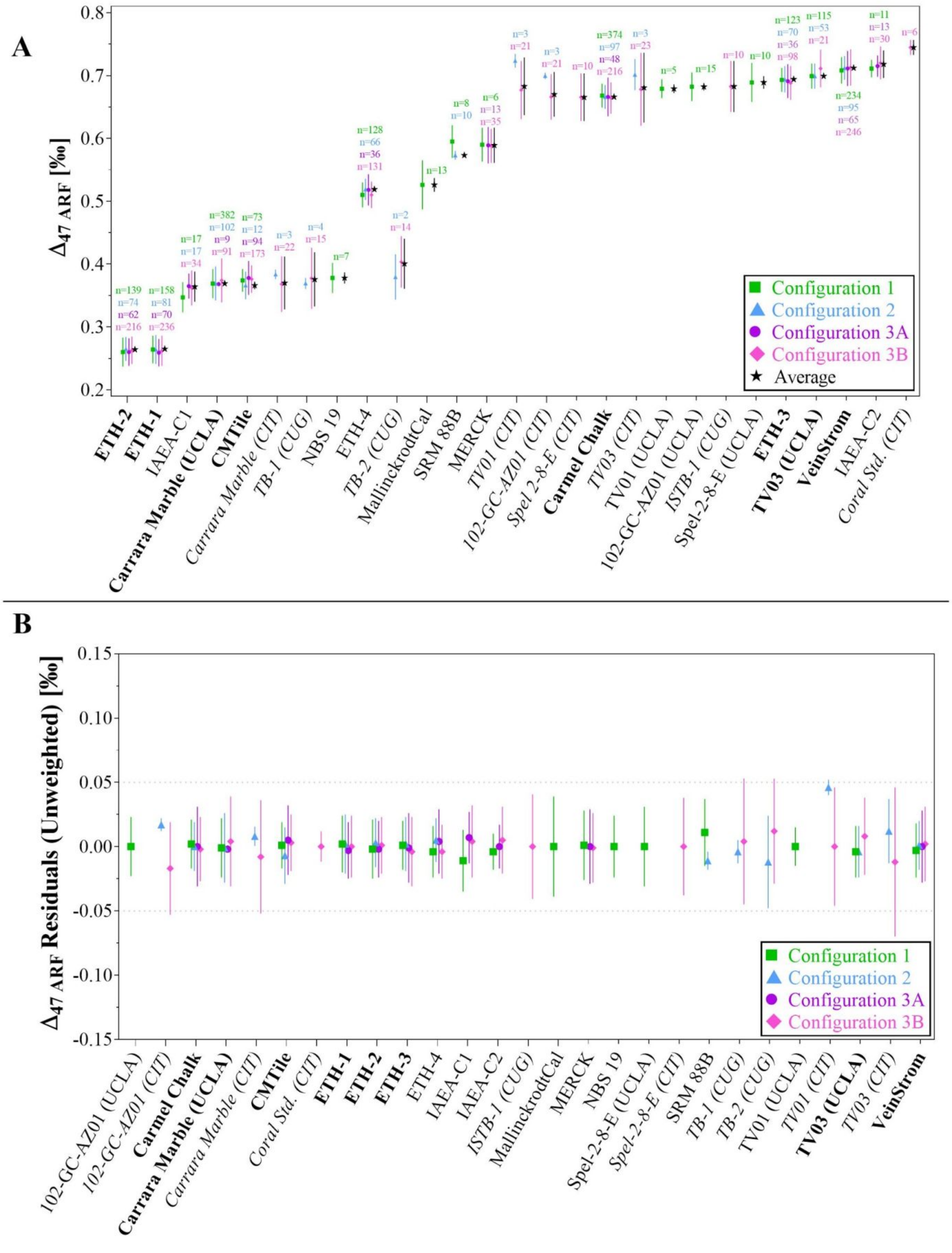
A
Δ47 ARF [‰]
0.8
0.7
0.6
0.5
0.4
0.3
0.2
n=139 n=74 n=62 n=216
n=158 n=81 n=70 n=236
n=17 n=17 n=34
n=382 n=102 n=9 n=91
n=73 n=12 n=94 n=173
n=3 n=22
n=4 n=15
n=7
n=128 n=66 n=36 n=131
n=2 n=14
n=13
n=8 n=10
n=6 n=13 n=35
n=3 n=21
n=3 n=21
n=10
n=374 n=97 n=48 n=216
n=3 n=23
n=5
n=15
n=10
n=10
n=123 n=70 n=36 n=98
n=115 n=53 n=21
n=234 n=95 n=65 n=246
n=11 n=13 n=30
n=6
■ Configuration 1
▲ Configuration 2
● Configuration 3A
◆ Configuration 3B
★ Average
ETH-2
ETH-1
IAEA-C1
Carrara Marble (UCLA)
CMTile
Carrara Marble (CIT)
TB-1 (CUG)
NBS 19
ETH-4
TB-2 (CUG)
MallinckrodtCal
SRM 88B
MERCK
TV01 (CIT)
102-GC-AZ01 (CIT)
Spel 2-8-E (CIT)
Carmel Chalk
TV03 (CIT)
TV01 (UCLA)
102-GC-AZ01 (UCLA)
ISTB-1 (CUG)
Spel-2-8-E (UCLA)
ETH-3
TV03 (UCLA)
VeinStrom
IAEA-C2
Coral Std. (CIT)
B
Δ47 ARF Residuals (Unweighted) [‰]
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
■ Configuration 1
▲ Configuration 2
● Configuration 3A
◆ Configuration 3B
102-GC-AZ01 (UCLA)
102-GC-AZ01 (CIT)
Carmel Chalk
Carrara Marble (UCLA)
Carrara Marble (CIT)
CMTile
Coral Std. (CIT)
ETH-1
ETH-2
ETH-3
ETH-4
IAEA-C1
IAEA-C2
ISTB-1 (CUG)
MallinckrodtCal
MERCK
NBS 19
Spel-2-8-E (UCLA)
Spel-2-8-E (CIT)
SRM 88B
TB-1 (CUG)
TB-2 (CUG)
TV01 (UCLA)
TV01 (CIT)
TV03 (UCLA)
TV03 (CIT)
VeinStrom

**Figure 4**

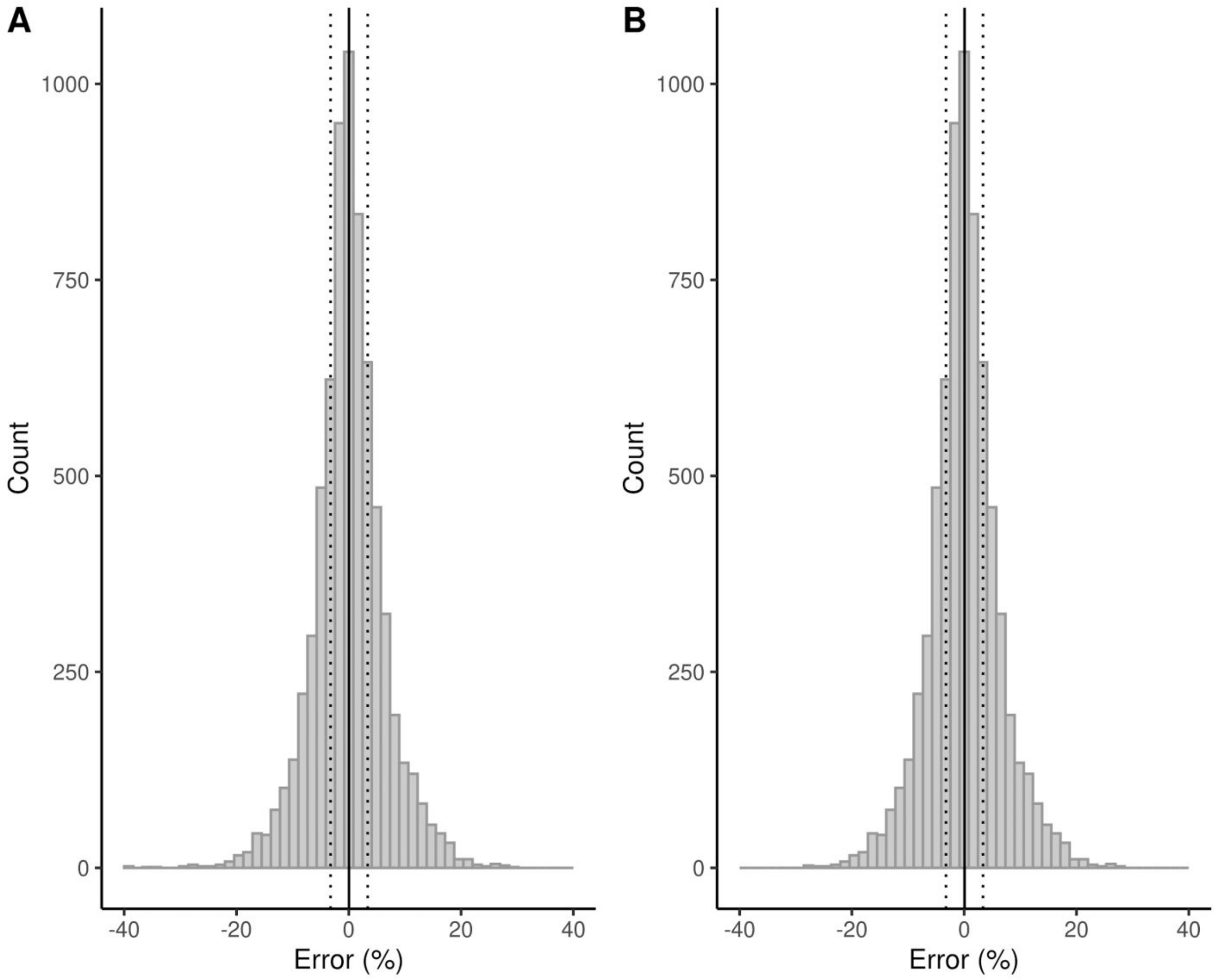

**Figure 5**

view

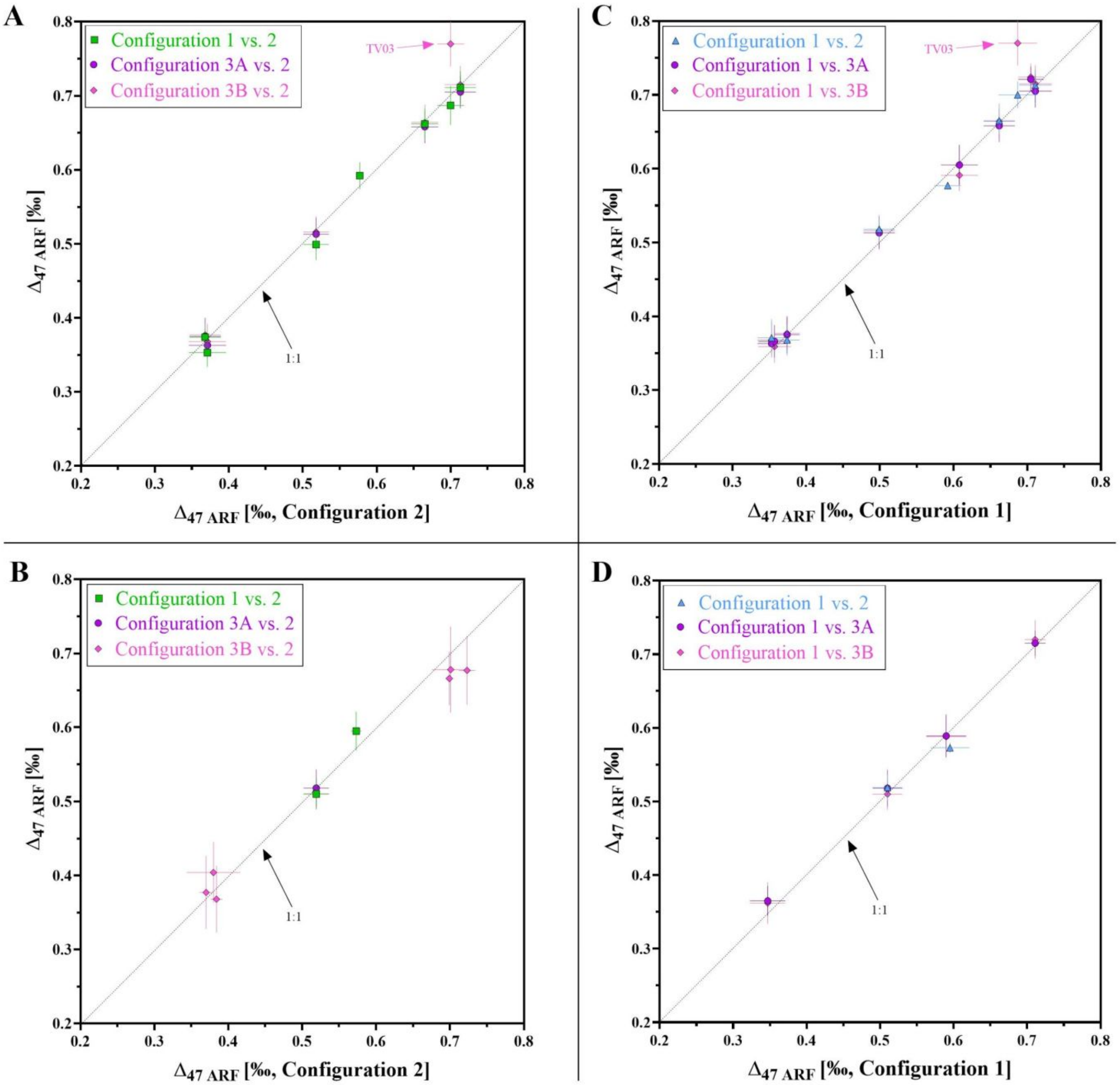
A
Configuration 1 vs. 2
Configuration 3A vs. 2
Configuration 3B vs. 2
TV03
1:1
$\Delta_{47\ \mathrm{ARF}}$ [‰]
$\Delta_{47\ \mathrm{ARF}}$ [‰, Configuration 2]
B
Configuration 1 vs. 2
Configuration 3A vs. 2
Configuration 3B vs. 2
1:1
$\Delta_{47\ \mathrm{ARF}}$ [‰]
$\Delta_{47\ \mathrm{ARF}}$ [‰, Configuration 2]
C
Configuration 1 vs. 2
Configuration 1 vs. 3A
Configuration 1 vs. 3B
TV03
1:1
$\Delta_{47\ \mathrm{ARF}}$ [‰]
$\Delta_{47\ \mathrm{ARF}}$ [‰, Configuration 1]
D
Configuration 1 vs. 2
Configuration 1 vs. 3A
Configuration 1 vs. 3B
1:1
$\Delta_{47\ \mathrm{ARF}}$ [‰]
$\Delta_{47\ \mathrm{ARF}}$ [‰, Configuration 1]
0.2
0.3
0.4
0.5
0.6
0.7
0.8

**Figure 6**

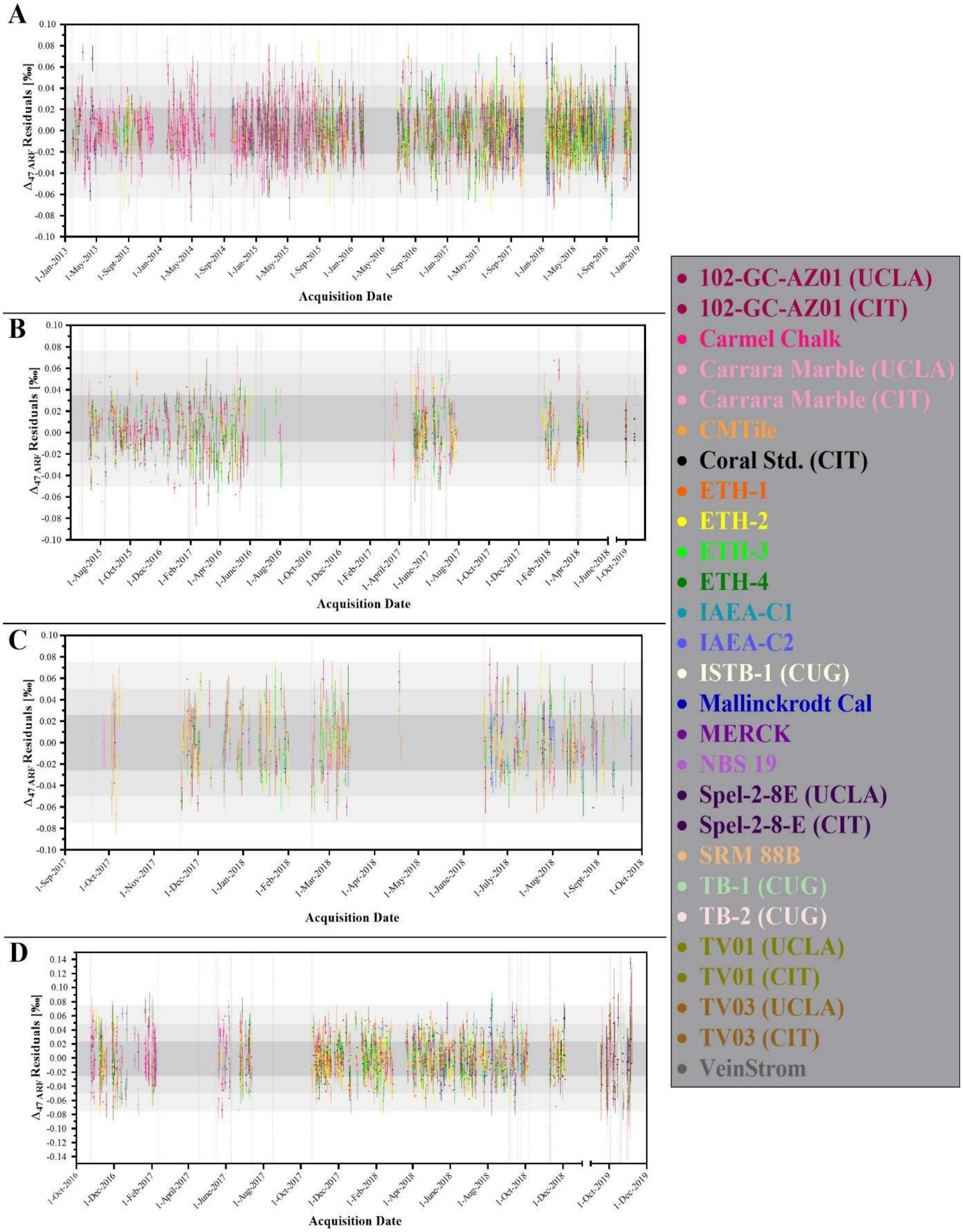
A
Δ47 ARF Residuals [‰]
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
1-Jan-2013
1-May-2013
1-Sept-2013
1-Jan-2014
1-May-2014
1-Sep-2014
1-Jan-2015
1-May-2015
1-Sep-2015
1-Jan-2016
1-May-2016
1-Sep-2016
1-Jan-2017
1-May-2017
1-Sep-2017
1-Jan-2018
1-May-2018
1-Sep-2018
1-Jan-2019
Acquisition Date
B
Δ47 ARF Residuals [‰]
1-Aug-2015
1-Oct-2015
1-Dec-2016
1-Feb-2017
1-Apr-2016
1-June-2016
1-Aug-2016
1-Oct-2016
1-Dec-2016
1-Feb-2017
1-April-2017
1-June-2017
1-Aug-2017
1-Oct-2017
1-Dec-2017
1-Feb-2018
1-Apr-2018
1-June-2018
1-Oct-2019
Acquisition Date
C
Δ47 ARF Residuals [‰]
1-Sep-2017
1-Oct-2017
1-Nov-2017
1-Dec-2017
1-Jan-2018
1-Feb-2018
1-Mar-2018
1-Apr-2018
1-May-2018
1-June-2018
1-July-2018
1-Aug-2018
1-Sept-2018
1-Oct-2018
Acquisition Date
D
Δ47 ARF Residuals [‰]
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
1-Oct-2016
1-Dec-2016
1-Feb-2017
1-April-2017
1-June-2017
1-Aug-2017
1-Oct-2017
1-Dec-2017
1-Feb-2018
1-Apr-2018
1-June-2018
1-Aug-2018
1-Oct-2018
1-Dec-2018
1-Oct-2019
1-Dec-2019
Acquisition Date
● 102-GC-AZ01 (UCLA)
● 102-GC-AZ01 (CIT)
● Carmel Chalk
● Carrara Marble (UCLA)
● Carrara Marble (CIT)
● CMTile
● Coral Std. (CIT)
● ETH-1
● ETH-2
● ETH-3
● ETH-4
● IAEA-C1
● IAEA-C2
● ISTB-1 (CUG)
● Mallinckrodt Cal
● MERCK
● NBS 19
● Spel-2-8E (UCLA)
● Spel-2-8-E (CIT)
● SRM 88B
● TB-1 (CUG)
● TB-2 (CUG)
● TV01 (UCLA)
● TV01 (CIT)
● TV03 (UCLA)
● TV03 (CIT)
● VeinStrom

Figure 7

**Table 1.** Description of each machine configuration in this study.

| | Configuration 1 | Configuration 2 | Configuration 3A | Configuration 3B |
|---|---|---|---|---|
| **Acid Digestion System** | Common Acid Bath | Common Acid Bath | Nu Carb | Nu Carb |
| **Acid Temperature** | 90 °C | 90 °C | 70 °C | 70 °C |
| **Mass Spectrometer Model** | Thermo 253 | Nu Perspective (2014 model) | Nu Perspective (2014 model) | Nu Perspective (2016 model) |
| **Regularly analyze equilibrated gases?** | yes | yes | no | no |
| **Mass-44 Beam Ion Intensity** | 16 V | 80 nA | 80 nA for large samples,<br>80-30 nA for small samples | 80 nA for large samples,<br>80-30 nA for small samples |
| **Integration Time** | 720 seconds | 1600 seconds | 1600 seconds for large samples,<br>1200 seconds for small samples | 1600 seconds for large samples,<br>1200 seconds for small samples |

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**Table 2.** Description of standards used in this study. Mean clumped ($\Delta_{47}$) and bulk ( $\delta^{13}C$, $\delta^{18}O$, and $\delta_{47}$) values in black are from Nu Perspective + 90 °C common acid bath (Config. 2, Analysis B3), and values in grey are the weighted averages calculated from the other configurations. Abbreviations for standards used in the text are shown in brackets. Standards from California Institute of Technology (CIT) or China University of Geosciences (CUG) are also indicated.

| Standard | Mineralogy | Origin | $\Delta_{47}$ (‰;CDES)[1] | $\Delta_{47}$ (‰;CDES)[2] | $\Delta_{47}$ S.D. | $\Delta_{47}$ S.E. | $\delta_{47}$ (%; WG) | $\delta^{18}O$ (%;VPDB) | $\delta^{18}O$ S.D. | $\delta^{13}C$ (%;VPDB) | $\delta^{13}C$ S.D. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **102-GC-AZ01 (UCLA)** | calcite | Vein carbonate from Grand Canyon | 0.690 | 0.682 | 0.023 | 0.006 | 2.663 | -15.1 | 0.089 | 0.4 | 0.073 |
| **102-GC-AZ01 (CIT)** | calcite | Vein carbonate from Grand Canyon | 0.706 | 0.699 | 0.005 | 0.003 | 2.040 | -14.0 | 0.046 | 0.6 | 0.035 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Carmel Chalk [CC]** | calcite | Chalk | 0.673 | 0.666 | 0.019 | 0.002 | 11.190 | -4.0 | 0.094 | -2.2 | 0.068 |
| **Carrara Marble (UCLA) [CM]** | calcite | Collected in Carrara, Tuscany, Italy. | 0.393 | 0.369 | 0.027 | 0.003 | 17.620 | -1.5 | 0.093 | 2.1 | 0.051 |
| **Carrara Marble (CIT) [CM]** | calcite | Collected in Carrara, Tuscany, Italy. | 0.407 | 0.384 | 0.008 | 0.004 | 15.602 | -1.8 | 0.066 | 2.0 | 0.026 |
| **CMTile** | calcite | Homogenized version of Carrara Marble (UCLA) | 0.390 | 0.366 | 0.022 | 0.006 | 17.714 | -1.5 | 0.060 | 2.0 | 0.024 |
| **Coral Std. (CIT)** | aragonite | Deep-sea coral | 0.746 | 0.745 | 0.012 | 0.005 | 18.538 | 2.7 | 0.096 | -1.8 | 0.121 |
| **ETH-1** | calcite | Carrara Marble, heated to 600°C at 155 MPa for 10 hours, sent from ETH Zurich | 0.294 | 0.264 | 0.023 | 0.003 | 16.772 | -2.2 | 0.078 | 2.0 | 0.031 |
| **ETH-2** | calcite | Reagent grade synthetic, subjected to same treatment as ETH-1, sent from ETH Zurich | 0.300 | 0.265 | 0.019 | 0.002 | -11.936 | -18.7 | 0.078 | -10.2 | 0.052 |
| **ETH-3** | calcite | Calcareous chalk from northern Germany, sent from ETH Zurich | 0.699 | 0.694 | 0.021 | 0.003 | 17.256 | -1.8 | 0.107 | 1.7 | 0.038 |
| **ETH-4** | calcite | Same reagent grade synthetic as ETH-2, but unheated, sent from ETH Zurich | 0.539 | 0.519 | 0.017 | 0.002 | -11.863 | -18.8 | 0.103 | -10.2 | 0.034 |
| **IAEA-C1** | calcite | Carrara Marble, from International Atomic Energy Agency | 0.387 | 0.363 | 0.025 | 0.005 | 17.515 | -2.3 | 0.072 | 2.5 | 0.034 |
| **IAEA-C2** | travertine | Collected in Bavaria. From International Atomic Energy Agency | 0.725 | 0.719 | 0.023 | 0.005 | 0.706 | -8.9 | 0.072 | -8.1 | 0.042 |
| **ISTB-1 (CUG)** | | | 0.691 | 0.683 | 0.041 | 0.013 | -1.515 | -8.5 | 0.023 | -10.7 | 0.049 |
| **Mallinckrodt Cal** | calcite | Synthetic, from Mallinckrodt Baker, Inc. | 0.550 | 0.526 | 0.039 | 0.011 | -39.128 | -21.9 | 0.112 | -40.4 | 0.091 |
| **MERCK** | calcite | Synthetic, from International Atomic Energy Agency | 0.608 | 0.588 | 0.028 | 0.006 | -39.100 | -15.6 | 0.065 | -42.0 | 0.039 |
| **NBS 19** | calcitic | Carrara Marble, from | 0.401 | 0.378 | 0.024 | 0.009 | 22.075 | -2.0 | 0.119 | 1.9 | 0.066 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | marble | National Bureau of Standards | | | | | | | | |
| **Spel 2-8-E (UCLA)** | calcite | Speleothem | 0.697 | 0.689 | 0.031 | 0.010 | 1.406 | -6.4 | 0.101 | -9.2 | 0.165 |
| **Spel 2-8-E (CIT)** | calcite | Speleothem | 0.675 | 0.666 | 0.038 | 0.012 | 1.953 | -6.2 | 0.048 | -9.5 | 0.700 |
| **SRM 88B** | dolomitic limestone | Collected from mine site near Skokie, Illinois, USA | 0.585 | 0.573 | 0.007 | 0.002 | 13.124 | -7.4 | 0.091 | 2.2 | 0.017 |
| **TB-1 (CUG)** | | | 0.395 | 0.369 | 0.009 | 0.004 | 5.438 | -11.6 | 0.344 | 1.8 | 0.120 |
| **TB-2 (CUG)** | | | 0.408 | 0.380 | 0.036 | 0.026 | -14.746 | -24.4 | 0.014 | -5.9 | 0.099 |
| **TV01 (UCLA)** | calcite | Travertine tile | 0.686 | 0.679 | 0.015 | 0.007 | 10.784 | -8.5 | 0.041 | 2.2 | 0.061 |
| **TV01 (CIT)** | calcite | Travertine tile | 0.727 | 0.723 | 0.011 | 0.006 | 9.977 | -8.2 | 0.191 | 2.7 | 0.125 |
| **TV03 (UCLA)** | calcite | Travertine tile | 0.704 | 0.699 | 0.020 | 0.003 | 11.308 | -8.4 | 0.099 | 2.6 | 0.055 |
| **TV03 (CIT)** | calcite | Travertine tile | 0.706 | 0.701 | 0.025 | 0.014 | 11.024 | -8.1 | 0.062 | 3.6 | 0.057 |
| **VeinStrom** | vein calcite | Shallow carbonate vein collected from Tempiute Mountain, Nevada | 0.719 | 0.712 | 0.019 | 0.002 | -1.510 | -12.6 | 0.092 | -6.2 | 0.054 |

[1] Calculated using equation from ref. 44: $^{new}\Delta_{47} = 0.048529 - 0.000165 \times \delta_{47} + 0.944081 \times {}^{old}\Delta_{47}$ (eq. Y), where $^{old}\Delta_{47}$ refers to the $\Delta_{47}$ values from Analysis B3 of this study.

[2] Calculated using published(13) values for ETH standards.

Review